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# A NON-SELECTIVE COLLECTOR FOR SAMPLING GASEOUS AIR POLLUTANTS

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Pittsburgh Coke and Chemical Company
Pittsburgh, Pennsylvania

1959

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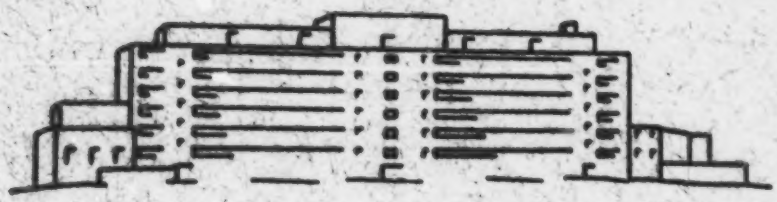

# A NONSELECTIVE COLLECTOR FOR SAMPLING GASEOUS AIR POLLUTANTS

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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service

# A NON-SELECTIVE COLLECTOR FOR SAMPLING GASEOUS AIR POLLUTANTS

(U.S.P.H.S. Contract No. SAPH-68345)

Prepared for

Air Pollution Engineering Research
Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

by the

Research and Development Department

PITTSBURGH COKE AND CHEMICAL COMPANY

Stanton B. Smith

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U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
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Division of Engineering Services

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

1959

FINAL REPORT

FOR THE SIX QUARTERS ENDING

DECEMBER 15, 1958

AIR POLLUTION RESEARCH PROJECT

on the design of

# "A NON-SELECTIVE COLLECTOR FOR SAMPLING GASEOUS AIR POLLUTANTS"

by the

Research and Development Department
PITTSBURGH COKE & CHEMICAL COMPANY

under

CONTRACT NUMBER SAPH-68345

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# FOREWORD

The Air Pollution Research and Federal Assistance Act (Public Law 159, 84th Congress, and Public Law 365, 86th Congress) authorized the Public Health Service, U. S. Department of Health, Education, and Welfare, to carry on a program of research and technical assistance related to air pollution. As a means of expediting the air pollution research effort under this program, the Act provides for research contracts. Contract research, as well as grant research, complements the activities carried on directly by the Public Health Service and by other Federal agencies.

Despite great progress in selective chemical tests for individual air pollutants, the bulk of organic vapors cannot be specifically determined by purely chemical means. Instead, fractionation methods such as vapor-phase chromatography must be used. These techniques demand a non-selective method of sampling. Adsorption has been used for this purpose, but has never been critically evaluated. For this purpose, a contract was initiated with the Pittsburgh Coke and Chemical Corporation for the design and evaluation of a portable adsorption sampler.

The report of the work conducted under this contract, contained herein, is published and made available for the information of individuals and organizations to whom it may be useful.

# A NON-SELECTIVE COLLECTOR FOR SAMPLING GASEOUS AIR POLLUTANTS


## ABSTRACT

The problem of collecting field samples of gaseous atmospheric contaminants has been investigated and a prototype collector design proposed which consists of two activated carbon columns in series, the second of which is refrigerated in dry ice. A field collector kit containing all accessory equipment for collecting 100-liter samples was designed and built.

Tests conducted on a specially constructed flow apparatus indicated the complete collection of methane and less volatile substances at concentrations of about 150 ppm. Strong oxidants cannot be handled since these react with the adsorbent. Good recovery of the adsorbed materials for analysis was achieved. However, further investigation of desorption and analytical techniques is required.



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## I. INTRODUCTION

### A. Statement of the Problem

The satisfactory collection of gaseous atmospheric pollutants for subsequent analysis constitutes a major problem in the characterization of smog atmospheres. To date a number of methods have been used, but none of them are completely satisfactory.

One approach has been the development of highly sensitive instruments for continuous analysis of a particular component in the atmosphere; for example, ozone and $SO_2$ may be continuously measured with such instruments. However, this approach is not practical for each of the tremendous number of trace compounds which are present in contaminanted areas. Many of these have never been positively identified, and there are probably thousands of substances present which have not as yet been detected.

Two general solutions to this problem have been freeze-out traps and adsorbent columns. Such devices should collect all significant gases and vapors, that is, all those substances which are not considered a part of the normal atmosphere. Ideally, these materials should be retained unchanged and should be recoverable for future analysis. The collector must also concentrate the materials so that they may be recovered in a form suitable for analyses by such conventional methods as mass spectrometry, infrared spectroscopy or gas chromatography.

A very rewarding approach to this problem has been the use of freeze-out traps, refrigerated with liquid oxygen, through which 100-liter air samples have been passed. From this type of collection, analyses by mass spectrometer have been successful in characterizing atmospheres contaminated with automobile exhaust gases in various stages of oxidation and with industrial effluents as well. By careful analysis of the spectrum it has been possible to identify a number of specific contaminants. (1)

However, this technique has several limitations. The use of liquid oxygen in the field is very inconvenient and quite impractical for general use on a countrywide basis. A preliminary processing of the sample for the removal of condensed oxygen, water vapor and carbon monoxide is also involved and time consuming. It would be highly desirable to have a general-purpose collector available which could be used easily in the field by inexperienced personnel, which would preserve the sample unchanged and in an easily transportable condition until the contaminants may be recovered from the collector for analysis.

Activated carbon columns have long been used for sampling contaminated atmospheres. However, the precise conditions required for complete collection and recovery of various types of materials have never been fully worked out. This is also true of other adsorbents such as silica gel, molecular sieves, alumina and the like, so that much research must be done in order to design a completely satisfactory adsorbent collector.

With this objective in mind the Department of Health, Education, and Welfare of the U. S. Public Health Service, through its Community Air Pollution Program made available to Pittsburgh Coke & Chemical Company funds for research in the design and testing of a non-selective collector for sampling gaseous air pollutants. (See Appendix A for Scope and Approach to Problem as outlined in Contract No. SAPH - 68345)

B. Advantages in an Adsorbent System

Some of the main advantages of an adsorbent collector should be as follows:

1. Complete collection even of highly volatile contaminants.
2. Practical temperature conditions for collection.
3. Simple transportation of samples in solid form without refrigeration.
4. Recovery of contaminants in highly concentrated form by the elimination of diluent air.
5. Preliminary fractionation or separation of various components in the column prior to analysis.

One cannot expect to completely achieve the ideal collector. However, if 100% collection of all materials cannot be attained, it will at least be satisfactory to know what percentage of efficiency can be expected under a given set of conditions.

C. Elimination of Diluents

The principal diluents in the atmosphere are nitrogen, oxygen and water vapor. In addition, of course, the rare gases are present and are of no interest in air pollution analyses. There is also a considerable quantity of carbon dioxide which can be easily measured and which is a normal though variable component of urban atmospheres. With an adsorbent collector of activated carbon, the nitrogen and oxygen should constitute no problem. In the freeze-out trap, considerable amounts of oxygen and nitrogen may be frozen out, whereas the temperature of the carbon collector may be kept high enough that significant quantities of these gases are not retained. Carbon has a particular advantage insofar as water vapor is concerned. Activated carbons, which are essentially ash-free have an extremely low affinity for water at humidities less than 40%. Almost any organic vapor is capable of displacing adsorbed water from the surface. However, the rate of adsorption is affected unfavorably by large quantities of water, and one should be careful to ensure that the humidity of the sample stream is kept low when traces of organic materials are to be adsorbed. In the case of very volatile materials such as methane and ethylene, it would probably be best to have a completely dry carbon since one needs all the adsorptive driving force obtainable to retain these materials at extremely low concentrations.

Carbon dioxide is quite strongly adsorbed and could constitute a problem worthy of investigation. It could be removed chemically but other acid gases of interest would probably also be removed. It should be possible to design the collector large enough to retain all the $CO_2$ as well as some of the lighter materials.

D. Substances to be Collected

The work by the National Bureau of Standards covering mass spectra of condensates from urban atmospheres delineates very well the scope of materials to be recovered. (1) A number of industrial atmospheres were sampled in Southern California, Washington, D.C., Louisville, Kentucky, and Detroit, Michigan. The distribution of mass spectrograph peaks in these samples indicates that molecular weights from 25 to 170 should include about 99.9% of the contaminants, exclusive of the diluent gases and the lighter materials not collected by freezing technique. Components having molecular weights higher than 170 should not be present to an extent exceeding about .01% of the collected material. All materials boiling below 350° should be included within this range.

Some idea of the amounts of material to be adsorbed may also be obtained from this work. In samples taken in Louisville, considerable industrial contamination was encountered. Total atmospheric pollutants, exclusive of diluents, methane and materials of molecular weight lower than 25, amounted to .2 to 1 ppm. Table I indicates the approximate mol per cent of some of the major contaminants of interest, including the contribution of normal traffic gas and oxidized traffic gas also.

1. Retention of Light Pollutants

It is quite significant that the acetylene ran as high as 15 mol per cent of the contaminants, and this is at the lower end of the weight series of substances which may be picked up in a freeze-out trap. The limit for collection of ethylene was stated to be about 30 ppm. and for ethane, 10 ppm. This indicates, then, that a carbon collector capable of picking up these more volatile materials might collect fairly large quantities of the lighter materials, including methane as well, provided the collector is designed to retain it. It is also stated that only that amount of acetylene in excess of .2 ppm. would be retained in a freeze-out trap. Consequently, considerably higher quantities of total pollutant might be collected with a more efficient collection system.

2. Reaction and Interaction of Collected Pollutants

The chemical reactivity of the various materials to be collected is of some concern and warrants investigation. In the first place, a carbonaceous adsorbent surface is capable of being oxidized and the formation of surface compounds or complexes is well known. It may be possible, however, to minimize this interaction if the collector is used at a sufficiently low temperature to prevent reaction. The principal gases of concern are $NO_2$ and ozone. Other highly oxidizing materials may also give trouble.

It is also desirable to prevent any interaction between the various adsorbed materials which might be catalyzed by the presence of the adsorbent or caused to react by virtue of mass action in the concentrated surface film. Here again, a low collection temperature may be desirable but reaction may not be entirely avoidable since the temperature of the collector must be raised for shipping.

A priori nothing definite can be said about the tendency of reactive substances to interact on an adsorbent surface. Each chemical entity would have to be studied in itself. However, on active adsorbents there is a strong tendency toward displacement of one adsorbed component by a more strongly adsorbed one. This would cause a natural fractionation or separation of the collected pollutants into zones, possibly reducing their tendency to interact considerably. In many cases strongly reactive pairs of materials may be separated by zones of inert material. Of course, as the pollutants are collected, the lighter materials must pass over zones of more strongly adsorbed substances but this contact would be brief, the localized gas concentration very low, and, if a refrigerant is used, the temperature would also be very low. Considerable resolution of interacting materials might then be attained before the collector is raised to ambient temperature. As the temperature is raised, one would expect to maintain this separation to a large extent.

E. Critical Factors in Collector Design

The size of an adsorbent collector must be determined by a number of factors.

1. The amount of air pollutant required for subsequent analysis.
2. The nature of the least adsorbable substance to be retained.
3. The minimum collection temperature allowable.
4. The volume of air sample desired (determined largely by the level of contamination expected and item 1 above).
5. The adsorptive activity of the activated carbon or other adsorbent used.

Though very little trouble is expected in adsorbing in low concentrations the materials containing four or more carbon atoms, a very critical situation may exist for the very volatile gases and vapors. In the case of the higher molecular weight substances the capacity of carbon, even at room temperature, is quite high and the progress of saturation, even in the ppm. concentration range, will be much slower than the flow of air sample through the collector. However, with the very light gases the concentration-capacity relationship (or isotherm) is much less favorable. For example, with methane the capacity of the carbon for this gas is almost directly proportional to its concentration. Therefore, the saturation front of air containing methane

would move at a fairly rapid rate through a collector just as a chromatographic wave moves through a gas chromatograph column. In other words, if methane-free air were continually blown through the collector containing methane, that gas which had already been adsorbed would soon be blown out of the collector. The rate of elution of methane can be considerably slowed by operating the collector at low temperature, but a critical volume limit is imposed even here. If it were desired to completely collect any carbon monoxide present, the situation would be even more unfavorable.

In Table II a number of substances have been listed in order of their critical temperatures since it has been observed that, in general, adsorbability follows this same order. Of course, one very notable exception is water which can be almost completely displaced by most of these materials. The adsorbability of CO is not quite as unfavorable as indicated by the table since experiments show that this is probably more adsorbable than oxygen.

F. Experimental Objectives

In light of the foregoing information the necessary experimental work is fairly well delineated and may be outlined as follows:

1. Determination of critical factors needed for design of a collector column.

   Various adsorbents would have to be investigated at different temperatures and the retention volumes determined at low concentrations.

2. Tests on a prototype collector column under a selected set of conditions.

   Once design information is available a decision must be made as to what is to be collected and the proper adsorbent and column dimensions selected. This column should then be tested on air streams containing very low concentrations of various contaminants of interest to see if collection is complete.

3. Design and construction of a portable prototype collector kit.

   Once the performance of a column collector has been found satisfactory under a known set of conditions, sampling equipment may be designed and constructed to perform conveniently in the field.

4. Development of an analytical scheme for recovered gases.

   Before a sample collector is of any value it must be shown that a practical degree of desorption and recovery may be achieved. This can only be done when analytical methods are available. Recovery of certain classes of compounds over a range of volatility can be established rather easily using conventional methods of analysis if the concentrations of the vapors are not too low.

   However, complete analysis of an air pollutant sample is quite another matter and a suitable subject for a separate investigation.

## II. EXPERIMENTAL PROGRAM

### A. Preliminary Experiments

When the program was started no specially built apparatus was available nor was the range of operability desired in such an apparatus known. Preliminary experiments were therefore necessary to:

1. Compare adsorbents.
2. Determine practical limits of collection of various gases.
3. Establish the requirements and design of specialized testing apparatus.

Attention was focused on a number of the light gases, i.e., methane, carbon monoxide, etc., since the selection of an adsorbent might reasonably be based on the retention of these materials. If such gases could be retained, there is relatively little doubt that collection of all less volatile materials would be quantitative.

Certain gases, namely NO and $O_3$, were recognized as possible interfering substances and tests were run to observe their behavior.

#### 1. Apparatus

##### a. Gas Chromatograph

The gas chromatograph built previous to the Contract by the Physical Section of the Research and Development Department was used with some modification. A schematic diagram of this unit is shown in Figures 1a and b. It has a very sensitive thermistor detector unit attached to a bridge circuit (Figure 2) and 1 MV recorder capable of responding to low concentrations of gas in the carrier stream. All working parts are mounted on the inside of the oven door and arranged as shown in Figure 1b.

This system had limitations since the only fractionation that could be applied to the gas sample was that which occurred in the adsorbent column. In order to make the system more versatile, a glass apparatus was built which could be attached externally at the two gas sample inlets by Burrell connectors as shown in Figure 1b.

##### b. Reversible Flow Column

This attachment, henceforth to be referred to as the Reversible Flow Column, RFC, is shown in Figure 3. It consisted of two 3-way stopcocks, A and B, attached to the Burrell inlet connectors, an interchangeable gas sample cell with ball and socket joints, C, a detachable U-shaped column, D, and a flow reversing arrangement consisting

of two 3-way stopcocks, E and F. Another 3-way stopcock, G, was used to permit flushing or evacuation of the sample cell. All stopcocks were fitted with spring retainers to withstand the pressure of the carrier gas. It was possible to employ a Linde Molecular Sieve column in the chromatograph to further separate mixtures coming from the Reversible Flow Column.

The purpose of the reversible flow feature was to permit a gas mixture to be swept into the column, allowed to remain there for a given period, and then swept in the reverse direction into the gas chromatograph. In the case of weakly adsorbed gases (having linear isotherms), the gas mixture, though partially resolved in the adsorbent column, would be reconstituted to its original composition (except for diffusion into a broader band) when it emerged from the column at the inlet and entered the chromatograph. This technique could be especially helpful in studying chemical interactions taking place within the column.

## 2. Adsorbents Studied

The materials selected as adsorbents are representative of several types that might be used to retain light gases and were picked simply to indicate which direction should be followed in a further search for an optimum adsorbent. They consisted as follows:

### a. Activated Carbons (See also Table III)

#### 1) PC&C Type BPL (Sample Stock No. 2)

This carbon is a general purpose commercial carbon for gas-phase adsorption, characterized by a moderately high specific surface (ca. 1000-1100 sq. meters per gram), an average pore diameter of about 18-20 Angstrom units and a moderately sharp pore size distribution as determined by water desorption isotherm and mercury porosimeter methods (2). (See Figure 4) It is a bituminous coal-base carbon with particularly low ash.

#### 2) PC&C Type HDL

This is a high density carbon of very retentive character by virtue of its finer average micropore diameter. Its specific surface is probably somewhat lower than BPL, but volume for volume it would have about the same surface area. The pore size distribution of this carbon is quite sharp, making it more specific for retention of small molecules. (See Figure 5) It is also a low-ash bituminous coal-base carbon.

3) Burrell High Activity Charcoal

Little is known about this activated carbon, but it is supplied expressly for use in the Burrell Kromo-Tog apparatus for precise fractionation of light hydrocarbons and other gases. It was suspected that this might have particularly favorable properties for retention of light gases. It is probably an activated coconut shell charcoal. Its pore size distribution curve is shown in Figure 6.

b. Non-Carbonaceous Adsorbents

1) Burrell Silica Gel

This gel is also supplied for use with the Kromo-Tog adsorption analyzer and should represent a high purity material with standardized properties.

2) Linde Molecular Sieve 5A

This material is typical of these molecular sieve synthetic clay-like materials, having very small internal cavities, in this case of approximately 5 Angstrom units in diameter. It was obtained as a sample from the Linde Company in 1/16-inch diameter pellets and crushed and screened to 35 x 60 mesh.

The data on various adsorbents is summarized in Table III.

3. Preparation of Columns

The columns were constructed of 1/4-inch O.D. copper tubing 24 inches long. They were coiled to fit the Dewar flask, weighed and then filled with the selected adsorbent by means of vacuum and weighed again. The total length of the packed adsorbent section was 22 inches. For the more critical tests the adsorbents were baked out at 400° C. while being purged with dry nitrogen or helium. The columns were connected to the reversible flow unit connections by short lengths of plastic tubing. The adsorbents prepared in this laboratory were ground to U. S. 35 x 60 mesh and dried at 140° C. for 24 hours before packing. The temperature of the columns was held constant by means of cooling mixtures in Dewar flasks, viz., ice water for 0° C. and dry ice-acetone for -78° C.

a. Gases Used

1) Hydrocarbons

The gases used consisted of Matheson Company high purity methane (99.0% min.), C.P. grade ethylene (95.0% min.), and instrument grade propane and n-butane (99.9% min.). No additional purification of these gases was carried out prior to use.

2) Coke Oven Gas

A convenient source of CO and methane is available in our plant-supplied laboratory gas lines. It is uncleaned gas and contains a high sulfur content in addition to the approximate composition given below.

| Gas | % by Volume |
|---|---|
| $H_2$ | 55 |
| CO | 7 |
| $O_2$ | 0.2 |
| $N_2$ | 7 |
| $CH_4$ | 25 |
| Other HC's | 3 |

$H_2O$ (saturated to outside temperature)

3) Carbon Monoxide

"High purity" carbon monoxide (99.5% min.) obtained from Matheson Company was used. (This was later found to be highly impure.)

4) Ozone

A Welsbach Ozonator was available in the Research and Development Department, and mixtures of oxygen and ozone were obtained from it and transferred to the laboratory in glass sample flasks and silica gel traps. The exact $O_3$ content is not known, but according to Welsbach instructions it should have been about 10-15% $O_3$ by volume.

5) Nitric Oxide

A lecture bottle of nitric oxide of stated 99.0% NO min. purity was obtained from Matheson Company. This later proved to be highly contaminated with CO, $N_2O$, $CO_2$ and other gases.

4. Procedure

a. Determination of Retention Time of Adsorbent Columns

When the columns had been connected to the chromatograph, the nitrogen flow and bridge current were turned on. The nitrogen pressure was regulated to between 7 and 10 psig. and the flow rate adjusted to 25-30 cc. per minute at room temperature and pressure. The bridge current used was 20 ma. (The thermistors used in this application had a room temperature resistance of 8,000 ohms.) It was found that it was not necessary to hold the cell block temperature constant in order to maintain acceptable base line stability. An empty "jumper tube" was substituted for the analytical column in the chromatograph.

The sample loop, C, was filled while the nitrogen carrier gas flowed through the by-pass valve. The carrier gas was then diverted to flow through the sample loop by turning cocks A and G and closing the by-pass shutoff, thus sweeping the sample into the column. The retention times were measured on the recorder strip chart from the injection of the sample to the maximum of the peak, and the retention volume found by multiplying this value by the flow rate.

b. Recovery Tests

In order to determine how readily materials could be recovered from an adsorbent, the analytical chromatographic column* inside the chromatograph was used in series with the collecting column, D. The retention time (volume) for this analytical column alone was first determined by the usual method. A sample of the gas in question was swept onto the collecting column, RFC, as described above with carrier gas flowing in the forward direction for a definite time. The stopcocks, E and F, were then turned to reverse the flow of the carrier gas and the sample was eluted from the collecting column into the analytical column. In such cases the observed total retention time should be the sum of twice the collecting time (duration of forward flow) plus the retention time on the analytical column.

* The analytical column consisted of 10 ft. of 1/4-inch copper tubing packed with 35 x 60 U. S. mesh Linde Molecular Sieve No. 13X.

B. Results of Preliminary Experiments

In Table IV are shown the results of preliminary tests made on oven-dried adsorbent using a filled 1/4-inch Cu tube, 22 inches long, containing approximately 10 cc. of adsorbent. Since fairly high retention volumes were obtained for methane on carbon, retention of the gas may be considered practical. These values indicate that careful study of the various grades of activated carbon is needed in order to minimize the volume of the collector. It was evident that only the 0°C. or -78°C. temperatures should be seriously considered.

A second series of more carefully controlled experiments was undertaken with previously weighed portions of the oven-dried adsorbent in 22-inch copper R.F. columns.

In addition to coke oven gas and NO, high purity CO and $CH_4$ were used. In Table V the weight of adsorbent and retention volumes are given for each gas adsorbed on the adsorbents. The volumes reported are at atmospheric pressure through the columns operated at about 30 psig. nitrogen pressure.

After running the retention values on the oven-dried samples, it was suspected that there might still be some adsorbed water or other vapors present which impaired adsorption of light gases. This could be especially true of the Linde sieve sample with its tremendous affinity for water at extremely low partial pressures. Both HDL and Linde 5A columns were baked out at 400°C.

1. Methane Retention

At -78°C. the retention volume for methane on activated carbons is quite large. For the HDL sample this amounted to 565 cc. per gram. The baking out of the HDL sample had a favorable but minor effect. It is significant that the three carbons studied varied from 364 to 608 cc. per gram for methane retention, indicating that the choice of the carbon is critical.

2. Carbon Monoxide Retention

Though the data for CO is not complete for all the carbons, the retention volume appears to be about 1/5 of that for methane, thereby requiring a container 5 times as large for complete retention. Tests with the other adsorbents were either inconclusive or incomplete and are therefore not reported.

3. Nitric Oxide Retention

It was hoped that nitric oxide might be retained since this gas plays an important role in the ozone cycle. Retention runs were attempted on the Matheson NO alleged to be 99.0% pure. Where retention times could be measured, a double peak was always encountered. An infrared analysis subsequently revealed the gas to be very impure. Large quantities of CO and $N_2O$ were found to be present as well as some unidentified gases. Though the first peak referred to in Table IV is probably NO and the second CO, the results were questionable.

An attempt was made to repeat the work on nitric oxide retention using pure gas. A review of the literature (3,4), however, revealed that even at -78°C. nitric oxide decomposes on carbon to yield an equilibrium mixture consisting of 96% nitrogen, 3% NO and 1% $CO_2$. These facts tied in well with our experimental observations and difficulties. In view of this, no further experimental work with NO was undertaken.

4. Ozone Retention

Fractionation of an oxygen-ozone mixture on a freshly dried 13X molecular sieve analytical column with helium carrier gas gave two peaks of unknown identity on the first run but on subsequent runs only one peak. When the performance of the column was then checked with a sample of air, no resolution was obtained, the conclusion being that it was deactivated.

Separation of oxygen from ozone was achieved at room temperature on a 7-foot long, 1/4-inch O.D. stainless steel column packed with silica gel. An ozone reservoir was first prepared by collecting the effluent from the Welsbach Ozonator in a glass trap containing silica gel held at -78°C. and noting the blue color of adsorbed ozone. The trap was attached to the sample loop of the chromatograph and both trap and loop were purged with helium to sweep out air. The temperature of the trap was then raised by removing the dry ice-acetone (-78°C.) bath in order to increase the concentration of ozone in the sample loop which was then closed. The ozone was then swept into the analytical column and two peaks were observed, an oxygen peak at 2¼ min. and ozone peak at 5-2/3 min. with a helium rate of 25 ml. per minute.

The effect of contacting carbon with ozone was investigated by passing a sample of ozone for one minute into a glass (Reversible Flow) column packed with 22 inches (3.111 grams) of 35 x 60 mesh HDL carbon held at -78°C. The sample was then reverse flushed into the silica gel column. The oxygen peak emerged at 3-2/3 min. (theoretical, 3½ min.) and the ozone peak at 6-3/4 min. (theoretical, 6-2/3 min.). However, an additional and reproducible peak at 10½ min. was observed which is interpreted to be the reaction product of ozone with carbon, either CO or $CO_2$.

5. Flushing of Adsorbed Air by Helium

Assuming complete collection of methane and all less volatile gases and vapors on a carbon column at dry ice temperature, it would be necessary to elute adsorbed nitrogen and oxygen to avoid excessive pressure build-up on raising the column to ambient temperature for ease in transportation. On the premise that such elution could be satisfactorily accomplished by flushing with helium at -78°C., experiments were undertaken to determine what additional amount of carbon would be required, beyond the minimum necessary for collection, to ensure no loss of methane in the process of elution.

Preliminary testing with a copper column containing 22 inches of Burrell HA char gave confusing results. A glass column was therefore packed with 22 inches of 35 x 60 mesh HDL carbon (3.111 grams), dried at 140°C. for several hours before packing. This column was attached to the RFC section with plastic tubing. With the column held at -78°C., the retention time for methane in air was determined to be 70 minutes at 25 ml. per min. air or a retention volume of 1750 ml., equivalent to 562 cc. per gram HDL carbon. This agrees with the value for HDL in Table V.

Many unsuccessful attempts were made to determine the retention time of methane in helium on this column at -78°C. The issue was confused by the fact that the helium was slightly contaminated. Continued work showed that the size of the methane peak, even at lowest sensitivity, was much greater than the extent of this contamination which was subsequently ignored. It was found that the retention time for methane in helium was 280 minutes, four times the retention time for methane in air.

A methane sample was then swept into the column in air for 35 min., corresponding to halfway penetration based on a 70-min. retention time. The column was closed, the apparatus flushed with helium and rezeroed with the column by-passed. The column was opened to the helium stream, and at lowest sensitivity a large air peak lasting approximately 25 min. was followed by a methane peak after 91 min. on helium purge. When the methane was allowed to penetrate the column for 47 min., equivalent to 2/3 of the column, it emerged after 62 min. on helium purge. Additional runs were made as follows:

| $CH_4$ Penetration Time (air) (min.) | $CH_4$ Emergence Time (helium) (min.) |
|---|---|
| 35 (= 1/2 way) | 91 |
| 43 | 60 |
| 47 (= 2/3 way) | 62, 78, 79, 67 |
| 49 | 67 |
| 50 | No $CH_4$ peak |
| 51 | No $CH_4$ peak |
| 53 | No $CH_4$ peak |
| 60 | No $CH_4$ peak |

It was concluded that the column could be 2/3 saturated with methane without loss on helium sweep but that beyond this point the situation becomes critical. Consequently, an additional amount of carbon equivalent to one-half of that for collection is required to ensure no loss of methane on eluting adsorbed air with helium at -78°C. To sample 20 liters of air at a retention volume of 562 cc. per gram for methane would require 35.7 g. HDL plus 17.8 g. for helium purge for a total of 53.5 g. HDL. Assuming an apparent density of 0.545 gram per cc., the volume of the collector would have to be at least 98 cc.

6. Air Pick-Up and Pressure Build-Up

A collector tube was fabricated from 3/4 inch O.D. stainless steel tubing, 12 inches long, with 1/4-inch O.D. stainless steel tubing welded to caps on each end. Valves were attached to the inlet and outlet tubing. The collector was filled with 32.3 grams of 6 x 16 mesh HDL carbon which had been dried at 140°C. for 24 hours and was then connected through a dry gas meter to a dry air supply. After flushing with dry air at room temperature the outlet valve was closed. A dry ice-acetone bath was placed around the collector, and dry air adsorbed at a pressure of one-atm. was metered through the dry gas meter. The volume of air adsorbed as read on the meter was on an average of 0.04 $ft.^3$. Failure to reach the theoretical value of .058 $ft.^3$, based on 25°C. and -78°C. adsorption isotherms, (5) caused us to suspect slippage in the meter at low flow rates; and this was subsequently confirmed by calibration. At a flow of 50 cc. per minute the meter read only about one-half this rate. However, calibration at a rate of one liter per minute showed that the meter functioned satisfactorily in the flow range in which it will normally be used.

After adsorption of dry air, the collector valves were closed and the dry ice bath removed. The pressure increased to a gauge reading slightly in excess of 100 psig. at room temperature. When the gas meter inlet was connected to the collector and the pressure released through the meter, a slightly larger volume was noted than that apparently adsorbed, giving further confirmation of meter slippage at the low flow rate on adsorption.

Adsorption at -78°C. was repeated, and the collector was then flushed with 5½ liters of helium prior to removing the dry ice bath. Pressure buildup amounted only to 20-30 psig. at room temperature, indicating a satisfactory purge of adsorbed air. The volume of helium necessary was computed by assuming that 3.111 g. HDL would require a 20-min. purge at a helium flow rate of 25 ml. per min., and therefore 32.3 g. HDL would require 5½ liters of helium. Purge time was varied from 5½ min. at one liter per minute to 13 minutes at the same superficial velocity (210 cm. per min.) as in the small tube without appreciably affecting pressure build-up.

7. Magnesium Perchlorate as a Drying Agent

A satisfactory drying agent must be capable of completely removing water vapor from the air stream without simultaneously adsorbing the gases or vapors of interest. Carbon dioxide was selected as a representative inorganic gas which is also acidic in nature. Benzene was selected as a representative organic vapor in the intermediate molecular weight range. A 6-mm. O.D. glass tube was packed with 10 inches (3.55 g.) of 35 x 60 mesh magnesium perchlorate previously dried at 140°C. for 2 hours. After packing, the $Mg(ClO_4)_2$ was redried in a stream of dry helium while the tube was held at 220°C. in a furnace. It was then cooled in dry helium and connected to the RFC section of the gas chromatograph. Dry air was used as the carrier gas, and the column was maintained at room temperature in a Dewar flask.

With the column by-passed, a sample of $CO_2$ was injected at an air flow rate of 25 ml. per minute. The $CO_2$ peak emerged in 1½ minutes. A sample of $CO_2$ was then passed through the column and emerged in 1-3/4 minutes. The peak was sharp, indicating little or no adsorption of $CO_2$ by $Mg(ClO_4)_2$. There is no reason to believe that other acidic gases would be more strongly adsorbed.

A sample of air saturated with benzene at 0°C. was injected at the same air flow rate with the column by-passed. It emerged in 11 minutes. When passed through the column it was retained for 12½ min. This indicates that the actual retention time in the column was only 1½ min., so that benzene adsorption is essentially negligible. Benzene was apparently retained for 11 minutes by partitioning on the stopcock grease in the system. Provision was then made to check the above data on benzene by substitution of glass stopcocks by Teflon plug greaseless stopcocks.

It was then demonstrated that the retention of benzene vapor by anhydrous $Mg(ClO_4)_2$ at room temperature was negligible. However, experiments were continued to determine the effect of polar functional groups, such as carbonyl and hydroxyl, on adsorption capacity.

Samples of air saturated at 25°C. with acetone and methanol were passed through the drying tube held at room temperature and 100°C. The experiments indicated considerable retention of both acetone and methanol at room temperature. However, at 100°C., deducting the retention time for the empty tube, the retention volume of acetone by 4 g. anhydrous $Mg(ClO_4)_2$ was only 125 cc.

Attempts were made to determine the retention time of methanol at 100°C. without success. Indications are that this material is retained but additional experimentation is necessary to confirm this.

## C. Discussion of Preliminary Experiments

The preliminary experiments indicated the possibility of completely collecting gases and vapors as high on the volatility scale as methane. Though ozone could be collected, its reactivity with carbon rules it out for collection. The effect of ozone on the other pollutants in the adsorbed state is an area for further investigation. There being other sensitive techniques available for the measurement of ozone in polluted atmospheres, it seemed wise to exclude this gas from further consideration. If found to interfere with the collection of other substances on carbon, it can be easily decomposed by catalysis at temperatures that should have little effect on the other pollutants. Likewise, nitric oxide was dropped as a possible candidate for collection. Nevertheless, the carbon collector still appears to be an attractive approach to gaseous air pollutant sampling because of its lack of selectivity and low reactivity toward non-oxidizing gases. Refrigeration below the temperature that can be obtained with dry ice, which is quite generally available in the field, is not necessary.

The flushing off of adsorbed air by helium without loss of collected light gases appeared practical, thereby effecting considerable concentration of the sample.

In order to more critically test the performance of a carbon collector column, a test apparatus capable of operating with very low concentrations of gas and vapors was required.

## D. Testing of Prototype Collector Columns

### 1. Efficiency Test Apparatus

The preliminary experiments indicated that an activated carbon column containing 55 grams of HDL carbon would collect and retain all the methane in a 20-liter air sample. However, this value was determined in a tube of high length-to-diameter ratio using rather high concentrations of methane. Also, it was not known whether the break-through time of a sustained flow of methane at a concentration of a few ppm. would bear any close relation to the retention time of a methane slug as already determined. It was expected that the break-through would be only slightly different than the retention time but this required experimental verification.

In order to obtain reproducible flow test data a rather elaborate test apparatus was designed and constructed. As more was learned about the problem, the design was altered but the finished apparatus resulted as shown in Figure 7 and in Plate I.

The apparatus consisted essentially of the following components:

a. Air purification train, A-C.

b. Mixing section for preparing predetermined dilute concentrations of selected gases or vapors in air, D-J.

c. Activated carbon column, with provision for heating or cooling, M.

d. Thermal conductivity detecting system, N. (See Appendix B)

e. Collection devices, O. (See also Figure 8)

2. Air Purification

The air purification train consisted of an MSA cartridge-type filter, C, to remove particulate matter such as dust and aerosols, a Hammond drying tower, A, containing indicating Drierite which was periodically regenerated as necessary, for removal of water vapor, and a large activated carbon trap, B, refrigerated at -78°C. for removal of $CO_2$ and other gases or vapors.

3. Mixing Section

The mixing section consisted of an inverted Aminco-Koegel Meniscomatic buret, G, for introduction of gases, and a diffusion cell, I, for introduction of condensable vapors into the test stream. The buret was modified by sealing a hypodermic syringe barrel to the tip and a three-way syringe stopcock, U, was attached. In order to restrict diffusion, the stopcock was connected to the line by means of a hypodermic needle, silver soldered into a Swagelok union. Stainless steel tubing (1/8 inch O.D.) was soldered to the stopcock side port for the purpose of purging and filling the buret. A mercury null manometer, H, was installed, one leg of which was connected to the buret and the other to the line to permit equalizing pressures in both parts of the system and so avoid surges in either direction through the needle and stopcock. In addition, a fritted glass disc was sealed below the level of the mercury in the leg attached to the buret. During flushing, the mercury level was depressed, exposing the disc and venting gas to the atmosphere. The manometer therefore served a dual purpose, although it was recognized that the presence of mercury in the system could lead to difficulty in dealing with sulfur gases. A series of glass bulbs, J, was provided to mix the gas stream thoroughly before reaching the carbon column or detector.

The diffusion cell, I, was constructed of glass with stainless steel Swagelok connections and plastic ferrules to circumvent the use of ground glass joints and the accompanying grease problem.

4. Carbon Columns

The activated carbon columns, M, were constructed of stainless steel tubing and glass respectively. The large collector was fabricated of 3/4-inch or one-inch O.D. stainless steel tubing capped on both ends. The end caps were drilled and soldered to the 1/4-inch O.D. tubing which connected the column to the stainless steel Dahl shut-off valves. The small collector was constructed of 6 mm. O.D. U-shaped glass tubing which had no valves attached but could be easily closed by plastic end caps.

5. Thermal Conductivity Detecting System

The thermal conductivity detecting system, N, was a Barnes Engineering Company unit, comprising a thermistor detector cell enclosed within an insulated bath whose temperature was proportionally controlled in the range from 50-300°C. The Wheatstone bridge circuit control unit operated from two 45-volt dry batteries in series. A reverse polarity switch and sensitivity switch capable to attenuating the output signal by a factor of 32 in powers of 2, were incorporated. The output signal was fed to a 1 MV Bristol strip-chart recorder.

6. Thermostatted Air Bath

The mixing section, flow and pressure controls and collection devices were located in an air bath. A 30" x 36" x 15" rack of Dexion steel was built with Plexiglass panels on front, sides and top. Valves and other assembly units were mounted on the rack or panels. The collection devices were mounted on the left side panel. The rear panel consisted of Masonite hardboard to which was attached a blower and 250-watt heater operated by a thermistor-actuated Sargent Thermonitor, P. Although temperature gradients possibly amounting to 2°C. could exist within the bath, the temperature at any point was constant to ± 0.05°C. at steady state. At the point of insertion of the thermometer, the temperature was 30 ± 0.05°C., and this could be attained within 20 minutes by virtue of the proportional control feature of the Thermonitor.

7. Flow-Pressure Controls

The purified air stream was pressure controlled by means of a Moore Nullmatic diaphragm-type pressure regulator, D, and then divided into a reference and test stream. This regulator effectively controlled the pressure in the mixing section and prevented pressure surges due to diverting the flow into the column.

The flow rate of the mixture was controlled by means of a Moore 63SU differential flow controller, L, which maintained a constant pressure differential across a needle valve, R, using the constant upstream pressure as a reference. A small portion of the main flow ahead of the column could also be diverted through the detector for calibration without increasing the flow through the mixing section. The main flow emerging from the flow controller, L, then passed either through the column or directly

to vent by means of the 4-way valve, W, with a small portion being diverted through the thermal conductivity detector, N, through 4-way valve, X. The reference air was divided into two streams through the reference and sensing sides of the detector, with a needle valve in each stream, Q, controlling the flow rates independently. A 4-way selector valve, X, immediately ahead of the sensing side of the detector made it possible to compare the response of purified air or column influent and effluent gas concentrations at will.

8. Displacement Section

Provision was also made for passing an organic displacing agent in a stream of helium into the small collector to remove and recover strongly adsorbed pollutants. The helium was passed through a saturator, K, containing the displacing agent at air bath temperature, then through a capillary flowmeter, $F_2$. The saturator could be by-passed if necessary.

9. Collection Devices

Figure 8 shows the collecting devices which were used to sample the gas emerging from the efficiency test line. They consisted of a pair of Toeppler pump collectors, A, filled with mercury and arranged with an overflow device, B, and submerged fritted glass inlet, C, to prevent any back pressure to the detector cell. Both the overflow traps and Toeppler bulb were fitted with glass float valves, D, to prevent overflowing of mercury.

The top outlets of the bulbs were connected to three-way cocks, E, which permitted admission of collected gas in either bulb to an evacuated liquid nitrogen cooled trap, F, gas chromatograph sample tube or infrared cell. It was also possible to pass a gas back and forth through a trap by by-passing the Hg overflow devices, B, and alternately raising and lowering the Hg leveling bulbs, G. A vacuum cock, H, permitted pumping down the lines and any collection device which is attached to the trap connections. Four-way cock, $I_1$, is shown in the position for sample collection, and cock, $I_2$, in the position for raising or lowering the mercury level.

E. Operation of the Efficiency Test Line

1. Calibration and Balancing

Before placing the line in operation, the following steps were taken. Flowmeters, $F_1$ and $F_2$, were calibrated on air and helium by wet test meter at room temperature and pressure. Care was taken to ensure that the gases entering the meter were saturated with water vapor in order to apply the appropriate pressure correction. The activated carbon tower, B, was regenerated at 200°C. in a stream of helium, cooled in helium and immersed in a dry ice-acetone bath (-78°C.).

Needle valves, Q, were adjusted to control the flow rate of air through the detector to 50 cc. per minute under normal operating conditions. The reading of the vernier on each valve was noted for future reference. It was observed that the detector cell was flow sensitive and a slight additional adjustment of the valves was necessary to equate the response on all three positions of the selector valve, X.

Start-up procedure consisted of controlling the air bath temperature to 30°C. and the detector cell temperature to the desired value. With cock, V, positioned to pass the flow through valve R, helium or air pressure was adjusted to read 6 psig. on gauge E. The flow rate on flowmeter F was set to one-liter per minute by means of needle valve R. Detector voltage was then adjusted to provide maximum response, and sufficient time was allowed for the cell to attain thermal and electrical stability.

2. Determination of Detector Sensitivity

The response of the detector cell to methane was determined as follows. Air flow was regulated to one-liter per minute with cock W in the by-pass position. The buret G plunger was lowered. Syringe stopcock U was turned to the filling position and methane from a cylinder was passed through valve S, cock U, buret G and then vented by means of a porous disc on manometer H. Methane flow was then interrupted by valve S, and buret and line pressures equalized on manometer H by raising or lowering the plunger. The counter was set to zero, stopcock U turned to delivery position and the motor-driven plunger actuated. Simultaneously, a stopwatch was started. Methane delivery rate was controlled to 0.1 cc. per minute at line pressure, approximately 3 psig. Since the air flow was metered at atmospheric pressure, methane flow rate had to be corrected to this pressure in determining the concentration in air.

A recorder deflection of 0.03 MV was obtained for a methane concentration of 120 ppm. Since the anticipated response to this level of contamination was at least 1 MV, it was apparent that it would be impossible to detect gas in the 1-10 ppm. range as originally planned. At maximum sensitivity, noise level was about .005 MV with a baseline drift of 0.3-0.4 MV per hour. This drift was not eliminated by prolonged operation at constant cell temperature and voltage.

At low speeds, the "meniscomatic" buret motor sometimes slowed down or stopped due to the drag imposed by the Veeder-Root counter. The manufacturer states that this deficiency may be remedied in later models by incorporating a more powerful motor. The minimum displacement rate for uniform operation was about 0.1 cc. per minute, the resulting concentration being 120 ppm. No attempt was made to operate at a lower rate due to lack of detector sensitivity at lower concentrations.

## 3. Determination of Break and Retention Volumes

### a. Theory

Two types of tests were run yielding values for the "break volume" and "retention volume" respectively. The break volume is that quantity of contaminated air which must pass continuously into a bed of adsorbent until the contaminant appears in the effluent stream. The "break" may be taken arbitrarily at any chosen percentage of the influent concentration. In general, at least 10% of this value must appear before one is certain of a break. Since the break-through wave is quite steep in most of this work and the break volumes large, it makes little difference what break concentration is chosen. Since the capacity of an adsorbent is concentration dependent, so also is the break volume. For long narrow columns the break volume is nearly proportional to the equilibrium capacity of the adsorbent (at the influent concentration) and inversely proportional to the influent concentration. This is apparent in the simplified Mecklenberg equation (6) as follows:

$$V_b = \frac{N_i}{C_i} (X_t - X_{ci}) B \qquad \text{Equation 1}$$

where: $V_b$ = Break volume in liters

$N_i$ = Capacity of adsorbent in equilibrium at $C_i$, g/g

$C_i$ = Concentration of influent vapor, g/l

$X_t$ = Total length of column, cm.

$X_{ci}$ = Length of "critical layer"; function of adsorption rate, cm. This is usually negligible in long columns at low $C_i$ and low gas velocity.

$B$ = Column loading, g. of adsorbent per cm. length.

Almost all carbonaceous adsorbents have capacity relationships (isotherms) of the following form:

$$N_i = k C_i^{1/n} \qquad \text{(Freundlich Equation) Equation 2}$$

where n is greater than 1. This equation gives curves concave to the concentration axis and therefore the concentration goes up proportionally faster than the capacity. As a result, the break volume $V_b$ decreases as the concentration increases.

It is therefore of interest to determine break volumes at concentrations somewhat higher than those expected in the field. It is comforting to keep in mind that the break volume will consistently increase as the concentration is lowered.

A special case results when the "n" in the Freundlich equation is 1. This situation exists with very weakly adsorbed gases such as methane when the temperature is fairly high. In the extreme low concentration region it has also been found that the isotherm (log-log curve) tends to become steeper thus approaching a slope of 1.

When n = 1, then $N_i = k C_i$ and by substituting in Equation 1 it is seen that the break volume becomes independent of concentration. This finding is the basis of gas chromatography theory and it implies that a point of any given concentration in the column will move at constant velocity through the column. Thus, material adsorbed during a brief period of high stream concentration might be desorbed by continual blowing of pure air, the adsorbed material being pushed along at this uniform rate. The rate of migration at a given rate of flow then yields a constant volume of gas, the "retention volume", which would be required to move the adsorbed material through the column. Retention volumes were thus determined for the lighter gases in order to see what maximum air volume-to-carbon ratio would be permissible for 100% retention.

Retention volumes are also of interest in studying the desorption of materials at elevated temperatures for recovery prior to analysis. Ideal desorption conditions would require a low retention volume permitting a clean elution of gas in a minimum volume without requiring a displacement agent, a situation to be realized only for the very light materials.

A retention volume determination still has some significance even when the Freundlich "n" is slightly greater than one. However, in this case when a zone of adsorbed material is eluted, the rate is concentration-dependent, causing slower and slower elution as the concentration falls, giving a very distorted adsorption peak, and a tailing zone following the emergence of the adsorption peak.

b. Experimental Runs

Four collector columns were employed in the course of the investigation. Two 3/4-inch O.D. stainless steel columns 11 inches and 22 inches long containing 32.3 grams and 55 grams respectively of 6 x 16 mesh HDL activated carbon and a one-inch O.D. stainless steel column 11 inches long containing 55 grams of the carbon were used to study the adsorption of $C_1$-$C_3$ hydrocarbons at -78°C. A 6 mm. O.D. glass column containing 1.5 grams 35 x 60 mesh HDL carbon was used to determine butane break volume at room temperature.

The column M was attached to the test line. Helium flow was regulated at one-liter per minute on flowmeter F, by means of needle valve R and flow controller L. Cock W was turned to permit helium to pass through the column which was heated to 200°C. The column was regenerated until the recorder indicated completeness of purging. This took approximately 20 minutes for the large column. For detection in helium, ample response was obtained at the lowest sensitivity of 32 MV full scale recorder deflection. The column was then cooled in helium. The stream

was changed to air at one-liter per minute on flowmeter F, and dry purified air passed through the column which was then cooled to dry ice temperature. Selector valve X was switched to all three positions, namely, reference purified air, column influent air and column effluent air and the response to each was zeroed on the recorder by adjusting cocks Q. The column was then by-passed by means of cock W, and selector valve X placed in the effluent position. The buret plunger was lowered, syringe stopcock U turned to the filling position and the buret purged with gas through valve S, which was then closed. Buret and line pressures were equalized by adjusting the plunger up or down until the manometer was balanced. The counter was set to zero, stopcock U was turned to the delivery position and the motor-driven plunger was actuated to deliver a gas concentration of 120 ppm. (0.1 cc. per minute). As soon as the recorder deflection for this concentration reached a constant level, cock W was opened to divert the mixture into the column and a mark made on the recorder chart. The column effluent response rapidly dropped to zero. Periodic checks were then made of the response to purified reference air by means of selector valve X to evaluate "zero drift". The effluent was more or less continuously monitored until a "break" was detected, as evidenced by the increase in effluent deflection from the zero reference level to the influent level. In cases where the break time exceeded 30 minutes, it was necessary to by-pass the column and refill the syringe whose delivery volume was 3.243 cc. full travel.

Determinations of retention volume were made by introducing about one-cc. of gas for one minute, then closing the syringe stopcock U. A determination of the retention volume of methane in helium at -78°C. was made to ensure completeness of retention of methane during helium sweep after collection. The retention volumes at 200°C. were carried out to properly assess the volume of gas that should be collected for maximum recovery on desorption.

4. Determination of Efficiency of Recovery

The technique consisted of passing a known concentration of gas (usually 120 ppm.) into the large column at -78°C. in a volume of air corresponding to two-thirds of the experimentally determined break volume of methane. Adsorbed air was then swept out with helium, the column temperature was raised and the desorbed gases were collected in the gas collection devices, Q.

The operation was as follows. The gas mixture was passed into the column by the method explained above for determining break volumes, and the column effluent was monitored. At the end of the prescribed period, the column was by-passed by means of cock W. The carrier gas stream was changed to helium at one-liter per minute, the detector voltage was adjusted and the deflections zeroed on all three positions of selector valve X at lowest sensitivity. Cock W was then opened and the column effluent deflection recorded. After purging with about 10 liters of helium, the air peak recorder deflection had come on scale and helium purge was complete. The column was by-passed by means of cock W and both column valves were closed.

The helium flow was shut off and cocks $T_1$ and $T_2$ turned so that the column effluent would pass into the collection devices, O, instead of to vent. Both Toeppler collector bottles (A, Figure 8) were filled with mercury by positioning the four-way cocks as shown by cock $I_2$. The bottles were then closed by means of three-way cocks, E, and the four-way cocks placed in position for sample collection as in $I_1$. The column exit valve was now opened, cock W opened, and the dry ice bath replaced by a 200°C. bath. The exit gases passed into one of the Toeppler bottles A. As soon as this flow ceased, the column inlet valve was opened and helium at a flow rate of 100 cc. per minute passed through the column into the collector bottle. When the first bottle was full, cock J switched the stream to the second bottle. Meanwhile, this effluent was monitored on the recorder and collection was continued until the deflection returned to the helium zero line. The stream was then vented by means of cocks $T_1$ and $T_2$, and four-way cocks $I_1$ and $I_2$ switched to the position for raising the mercury level.

Infrared cell, F, was attached, (see Appendix C for diagram), evacuated through cock H, and the vacuum system cut off. Three-way cocks E were turned to allow the contents of the bottles to fill the infrared cell until mercury completely filled the bottles. The cell valves were then closed and the cell was transported to the Baird IR spectrophotometer. The contents of the bottles could be similarly transferred to an evacuated refrigerated trap.

The one-meter path infrared cell was calibrated by introducing a known volume of gas in a stream of helium into the collector bottles and then transferring this mixture to the infrared cell by the technique already described.

Preliminary attempts to analyze the contents of the collector bottles by trapping in an activated carbon trap refrigerated at -78°C. and desorbing at 200°C. into the Burrell "Kromo-Tog", K II, gas chromatograph were unsuccessful. The results were 1/5 of those obtained by direct injection of the same volume of gas into the "Kromo-Tog". It is felt that a discrepancy of this order of magnitude could only be due to instrumental difficulties and not to failure to desorb the gas quantitatively. No difficulty was experienced in reconciling infrared results with those obtained by direct introduction of a sample into the cell.

Without doubt the gas chromatographic method could have been used successfully if the calibration and injection techniques had been completely worked out. Unfortunately, insufficient time was available to accomplish this.

## F. Experimental Results

The retention and break volumes experimentally determined and the corresponding specific retention and break volumes are indicated in Table VI. The specific retention volume of HDL activated carbon at -78°C. for methane as shown in Runs 4 and 6 appears to be constant at 565 cc. per gram of carbon. The actual retention volume for methane is therefore independent of flow rate, particle size and cross-sectional area of the bed within the range of experimental variables tested. This range covers carbon weights from 3.11 grams to 55 grams,

flow rates from 25 cc. per minute to 11. per minute, particle size from 35 x 60 mesh to 6 x 16 mesh, and cross-sectional areas from that of a 6 mm. O.D. tube to a one-inch O.D. tube. The break volume for 200 ppm. is essentially the same as the retention volume (Runs No. 1 and 2) as expected for $CH_4$ in air because of the linear isotherm.

Significantly, it was observed that the wave front of methane at low concentration is fairly sharp. In those instances where the carbon was reactivated in helium, the break volumes in the 3/4-inch O.D. column closely match the retention volumes. Discrepancies were noted, however, when the carbon had been regenerated in air (Runs No. 6 and 7) and when the length of the column was reduced (Run No. 5). Regeneration in air instead of helium appears to reduce the break volume, possibly because of adsorbed $CO_2$ remaining on the surface. Also, there appears to be a minimum column length, associated with a given weight and particle size of carbon, below which the effects of channeling or diffusion become important. The length of the one-inch O.D. column packed with 55 grams carbon was probably less than this minimum and resulted in methane breaking through considerably before the true retention volume was reached.

It seems safe to conclude from the results that a 3/4-inch O.D. column packed with 6 x 16 mesh HDL carbon will retain methane at concentrations of 100 ppm. or less in 31 liters of air. Since the intention is to sample not more than 20 liters of air through the column, followed by a 9 liter helium sweep, it is unlikely that any methane or higher molecular weight compounds would escape. The retention volumes of methane, ethylene and propane at 200°C. indicate that both methane and ethylene can be recovered in one-liter of desorbed gas by forward flushing, whereas at least three one-liter collections would be necessary to catch the desorbed propane.

The small column, 6 mm. O.D., was tested only for butane, since this would probably be the lightest gas that it would be required to hold quantitatively. A fine mesh carbon was used so that a short column of 1.5 grams could be used without fear of channeling. Even this small column required 150 liters to break at the 100 ppm. level. Lower concentrations would yield even larger break volumes, indicating that none of the butane present in a 150 liter sample would penetrate the small column. In view of this result it is also probable that most of the propane in 100 liters would also be retained in the small column at room temperature. Further tests should be made to determine what portion of $C_2$ and $C_3$ gases would be retained on the small column when it is placed ahead of the refrigerated column.

G. Efficiency of Recovery

Table VII shows the recovery and calibration runs for methane, ethylene, propane and benzene. Runs marked "reference" indicate only the measurement of a known volume of gas into the IR cell for calibration by the same techniques as used in recovery tests.

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The data in Table VII shows that methane and ethylene can be desorbed at 200°C. with helium and recovered in approximately 90% yield. Difficulty was experienced with forward flushing techniques when attempting to recover propane by repeated one-liter collections. However, the first attempt to reverse flush propane (Run No. 16) with helium at 200°C. gave quantitative recovery. This immediately suggested the possibility of obtaining the same recovery by reverse flushing of methane or ethylene.

Whenever the adsorption zone has penetrated the column only a short distance, as would be the case with the $C_2$ and higher hydrocarbons, it will be more efficient to reverse flush during desorption, thereby minimizing the dilution of the recovered vapors by the sweeping gas. Nevertheless, the retention volume for propane at 200°C. is 52.8 cc. per gram indicating that at still higher molecular weights elution would be very slow. In such cases a displacing agent of high molecular weight will probably be necessary.

Failure to recover methane and ethylene quantitatively is not considered at this time to be an indication of any real limitation on recovery. As the technique is more fully developed and mastered, quantitative recovery is confidently expected even though greater difficulty might be expected when lower gas concentrations are collected. Experimental difficulties are bothersome but there appear to be no fundamental restrictions interfering with complete recovery.

The benzene recovery run No. 17 employed a helium stream saturated with chlorobenzene as a displacer. A sharp clean separation of the benzene could be detected on the thermal conductivity detector. However, the displacer used was not sufficiently pure for ideal operation since light contaminants appeared between benzene and the displacer itself.

Further recovery investigations should include the use of displacers not only to make elution quick and quantitative but to yield the eluted vapors in concentrated form readily suitable for analysis.

H. Design of Field Collector Kit

On the basis of preliminary information on retention times of gases on activated carbon at various temperatures it appeared practical to design a collector kit for field operation. The principal criteria of design for such a unit were:

1. Accuracy and reliability
2. Compactness, portability, ruggedness
3. Simplicity of operation
4. Easy availability of accessory supplies, i.e., refrigerants
5. Simple transport and storage of collected samples
6. Reasonable cost

The flow sheet for the kit in its final form is shown in Figure 9. The components in line of flow consist of the following: A-filter, B-drying column, C-a small activated carbon column, E-dry gas meter, H-large activated carbon column, $I_1$-air flowmeter, J-vacuum pump, K-helium cylinder, L-pressure regulator and $I_2$-helium flowmeter. This flow sheet was altered several times in the design stage but was finally constructed as shown in Figure 9. Front and back views are shown in plates II and III.

The pump, air filter, valves and small tubes were mounted on a Plexiglass panel and the entire assembly including Dewar flask, helium cylinder and dry gas meter was erected within a Unistrut framework so that the instrument is portable. At present it is designed to operate on 115 V Ac but can easily be adapted to operate from a 12 V automobile storage battery. The unit so constructed weighs approximately 60 pounds.

The drying tube, 200 W. cartridge heater and thermostat are contained within an aluminum block to increase the heat capacity of the system. Two interchangeable thermostats are provided, one set at 200°C. for regeneration of the anhydrone, the other at 100°C., at which temperature water vapor should be picked up without serious adsorption of organic compounds. A pilot light in parallel with the heater indicates when the drying tube has reached the prescribed temperature.

An itemized list of parts is included in Appendix P.

1. Size of Air Sample

The sizing of the collector components depended on several factors as previously mentioned. Ideally, the size of the air sample should be set by the sensitivity of the analytical methods to be used on the recovered sample. Sinch techniques for complete analysis are not now available, certain assumptions were made. Methods of analysis most likely to be employed are: a) gas chromatography, b) mass spectrometry and c) IR or UV spectrophotometry. All of these are capable of handling samples of a few micrograms. For the analysis of vapors in the $C_3$-$C_8$ range, it appeared that 100 liters would be a reasonable sample. A material of molecular weight 80 in a concentration of .2 ppm. would yield about 70 micrograms of sample. Samples of this size have been analyzed in detail by mass spectrometer by a number of investigators (1).

In the case of light gases higher concentrations can be expected and these are more easily handled analytically so that a 20 liter sample may be considered practical.

2. Choice of Adsorbent

Of the several adsorbents tested, activated carbon, silica gel and Linde Molecular Sieve, the highest specific retention volume at -78°C. for methane was obtained with an activated carbon of fine porosity. The carbons tested varied by as much as 30% and it was decided that the most retentive carbon, HDL, should be used for the collection of light gases so as to minimize the size of the collector.

3. Sizing the Carbon Columns

a. Collector for Light gases

The amount of carbon required depends upon the lightest gas to be completely retained. A sufficient amount must be used to retain all the contaminant in the sample volume plus that required to prevent loss when helium is used to sweep out the adsorbed air. The helium sweep is thought desirable to prevent pressure build-up in the closed collector column when warmed to ambient temperature for shipment. Though the collector can be made strong enough to hold the pressure, it was thought desirable to flush in order to lessen the possibility of leakage and to concentrate the sample. (When the adsorbed gases are subsequently desorbed for analysis they will be diluted by only a few cc. of helium rather than with several liters of desorbed air.)

Since it is impractical to collect CO because of its very low retention volume at -78°C. and collection of NO is impractical because of its reactivity, methane was chosen as the lightest gas to be completely collected. For a 20 liter air sample using the retention volume of 562 cc. per gram (32.2) grams would be required for complete collection and another 50% required to allow for flushing plus a safety factor giving a total of ca. 55 grams.

The length-to-diameter ratio should also be specified as well as the particle size range of the adsorbent. A high length-to-diameter ratio is desirable to minimize channeling and uneven saturation of the column. The narrower the column, the sharper will be the separation of zones of adsorbate in the bed. The first column made for test purposes was constructed of 3/4-inch O.D. stainless steel tubing but contained only 32.3 grams of carbon. A second one was constructed of one-inch O.D. stainless steel tubing which was the size required to hold the carbon within the length that could be accommodated in the most convenient commercially available Dewar flask. However, experiments with this column indicated lack of sharpness in the break-through curves for methane and it was decided to use a double collector, H, consisting of two sections of 3/4-inch diameter tubing in a U-shaped arrangement, each containing 27.5 grams of HDL carbon in a 12-inch packed section held in place by glass wool and Swagelok caps.

For simplicity a commercial particle size range, 6 x 16 U. S. mesh, was used since this factor did not appear critical in a column of this diameter.

b. Collector for Condensible Vapors

If 100 liters of air were to be sampled for the $C_4$-$C_8$+ materials, a separate collector must be constructed for them. Such substances are very easily adsorbed but recovery may constitute a considerable problem. The collector in this case should be kept as small as possible

so that desorption will be made easy. Since all light vapors are to be picked up by the large refrigerated column, one can arbitrarily decide what gases one should collect completely in the small collector. Since this is to sample 100 liters, one should avoid, if possible, the complication where a material is adsorbed partly in the small and partly in the large column. If the size of the small one is properly chosen, the first 80 liters should saturate it with respect to the lighter gases and the 20 liter sample to the large collector will be truly representative of the light contaminant composition. These materials may then be ignored in the small collector where collection will not be quantitative.

The exact amount of carbon required was not determined but 1.5 grams of fine 35 x 60 mesh HDL was decided upon. A check was made of the retention of butane at 100 ppm. at 25°C. The break came at 150 liters showing that butane would be completely collected from a 100-liter air sample by 1.5 grams of carbon.

4. Filter for Removing Particulate Matter

Since this collector is to sample the gaseous pollutants only, means must be provided for filtering out all suspended particles. A high efficiency dust filter, A, with negligible adsorption for gases was found in the Fiberglass paper type ultra-filter developed for gas masks. A handy readily adaptable device was found in the form of a commercially available instrument line filter made by Mine Safety Appliance Company which uses cheap, replaceable filter cartridges. The convoluted shape of the filter fabric gives a large filter area and very little resistance to air flow.

5. Drying Devices

Water is known to have a deleterious effect on the adsorption of vapors by carbon, especially at very high humidities and for highly volatile vapors or gases. The drying agent used must be completely selective for water and must not adsorb other substances appreciably, even those of high molecular weight. The agent should also be neutral and chemically inactive so as not to react with any component. This ideal may be impossible to achieve but may possibly be approached.

Favorable performance was reported for magnesium perchlorate, $Mg(ClO_4)_2$, or anhydrone at 100°C. by P. West (7) when benzene and other vapors were collected through it. This material, anhydrone, was thus chosen for initial trials. The elevated temperature was used to prevent any adsorption of vapors. Being a crystalline material, its surface area should be low and it should also be reasonably neutral. Even at 100°C. it is reported to have a very high affinity for water (8). The size of the tube, B, was chosen so that all the water in several 100-liter air samples of summer air at 100% humidity could be handled without requiring regeneration. However, this capacity was not tested experimentally.

Some experiments, however, indicated that $Mg(ClO_4)_2$ may not be suitable for alcohols. Further experiments are required to confirm this. If true, another material; e.g., Drierite, anhydrous calcium sulfate, might be employed at a somewhat elevated temperature if necessary in the same drying agent container and heat control device.

An aluminum heating block, M, containing a Fenwal thermoregulator and cartridge heater offers a reasonable solution to the problems of uniform controlled temperature and portability.

6. Gas Flow Measurement

If the measurement of air pollutants is to be quantitative, an exact measurement of the air sample must be made. Continuous flow reading devices can seldom be read accurately and almost never can be held at a constant setting over prolonged periods. The best flow integrating device therefore was considered to be a displacement-type dry gas meter, E. Good accuracy should be obtainable if the meter operates at a flow rate high enough to prevent slippage past valves and at a known pressure.

It has a particular advantage in this application since the refrigerated carbon can adsorb several liters of air when it is just opened. The meter can be placed ahead of the collector, H, and will truly measure the air passing into the collector column, though it must be corrected for the operating pressure difference below atmospheric pressure. It will also measure correctly the air passing through the small collector placed upstream since no appreciable adsorption of air will take place at this point. Placing the meter after the small carbon column, C, will also protect the meter from any condensible vapors which might contaminate or corrode it. All light gases should pass through it quantitatively. The 80-liter collection into the small column will suffice to completely flush out the meter so that the large column sample will be representative. It is therefore possible to measure the air sample with a high degree of accuracy and to stop the flow of air at any predetermined point by reference to the meter reading. A conventional floating ball flowmeter, $I_1$, was also placed in the line to show the approximate instantaneous sampling rate.

7. Helium Flushing

The helium flushing facilities consist of a small high pressure helium tank, K, reducing valve, L, shut-off valve and metering floating ball flowmeter, $I_2$. This system permits a known volume of helium to pass through the refrigerated column to remove adsorbed air after the sample has been collected. This prevents the build-up of pressure in the closed collection column when the refrigerant is removed.

I. Operation of the Field Kit

1. Sampling

Starting with all the components in place as shown in Figure 9, and the drying agent at temperature, dry ice refrigerant surrounding the sampler,

and all valves closed, the pump may be started. A reading is taken on the dry test meter, and valve $F_1$ fully opened. The pump should be run at reduced speed so as to prevent overheating. It may be adjusted by the variable transformer to draw, with the valves fully open, slightly over five liters per minute. The metering valve $I_1$ on the pump J may be adjusted to give the prescribed rate of flow, e.g., five liters per minute. The air being sampled is then drawn through the aerosol filter, drying agent, small carbon sampler, C, gas meter and flowmeter by the pump J. An exact volume of air may be sampled for the less volatile pollutants by reference to the meter reading; e.g., 80 liters may be passed through the system.

While this air is being sampled, the large carbon collector H is being cooled to dry ice temperature; and, in order to prevent a sudden suction of air into the collector when the valves are opened, helium may be admitted before placing the collector on stream. The cylinder valve may be opened, the pressure set at one psig., the regulator needle valve L and flowmeter valve $I_2$ opened. The upstream collector valve, $G_1$, may then be cracked to admit helium.

After sampling 80 liters of gas for high boiling materials, a smaller quantity, e.g., 20 liters, may be taken through the small collector and large collector in series. The helium flowmeter valve $I_2$ is closed, valve $F_1$ closed and valves $F_2$ and $G_2$ opened. Flow may then be adjusted on the pump flowmeter $I_1$ and flow continued until an additional 20 liters is registered on the meter E. It is important that not more than the prescribed volume be taken since excess carbon must be available in the collector to allow for migration during flushing with helium. Valves $I_1$ and $F_2$ are then closed and the unit is ready for flushing. The small collector may be removed, capped and made ready for shipment.

2. Flushing of Large Collector

Helium flushing is necessary to remove adsorbed air so that the cold bath may be removed without building up high pressures in the collector. With valves $F_1$ and $F_2$ closed and $G_1$ and $G_2$ opened, valve $I_2$ may be fully opened and the valve $I_1$ used to throttle the helium stream through the collector at a slow prescribed rate, e.g., one liter per minute, as read on the flowmeter $I_2$. Since the amount used is critical, an accurately calibrated flowmeter must be used and the prescribed volume, e.g., nine liters, must be measured by timing the flushing at a constant known rate of flow. Helium is not passed through the meter E since considerable flushing would be necessary to purge air and also considerable slippage could be expected with this gas. After this volume has been passed the pump can be stopped, helium cylinder shut off and the main shut-off valves $G_1$ and $G_2$ tightly closed. The collector may then be disconnected from the system and removed from the bath for shipment to the lab for analysis.

## III. SUMMARY AND CONCLUSIONS

Tests of the retentive power of various adsorbents indicated activated carbon is superior to silica gel and molecular sieves for the non-selective collection of air pollutant gases. When dry ice is used as a refrigerant on a carbon

column it is possible to collect methane and all gases of lower volatility in a sample of reasonable size. Certain oxidising gases such as NO, $NO_2$ and $O_3$ appear to react with activated carbon and must be considered separately.

Columns of various sizes were tested over a wide range of gas concentrations and a column containing 55 grams of Pittsburgh HDL activated carbon chosen to sample 20 liters of air for light contaminants. A smaller column for operation at room temperature containing 1.5 grams of the same carbon may be used ahead of the refrigerated column to collect $C_4$ and higher compounds from 100 liters of air.

A field collector kit was designed which affords a preliminary filtration and drying of the air sample, positive displacement measurement of the sample volume, continuous flow measurement and mechanical pumping of the air sample. A helium flushing system for the refrigerated collector is also provided to remove the bulk of air adsorbed from the sample.

Prototype columns were tested satisfactorily for retention under exaggerated test conditions on selected hydrocarbon vapors.

A few recovery runs indicated that good recovery can be confidently expected after further experimental development of recovery techniques.

## IV. RECOMMENDATIONS

Since several areas mentioned in the scope of this "best efforts" contract were not investigated, further work is recommended in these areas.

1. The collector kit should be tested under field conditions to gather operating know-how and indicate design revisions where needed.

2. The collector column should be further tested on gases and vapors other than hydrocarbons for both retention and recovery.

3. Drying agents other than magnesium perchlorate should be tested in the hope of finding a completely non-adsorbing substance for water removal.

4. Desorption techniques including the use of displacement agents should be explored to yield a practical method of quantitative recovery.

5. An exhaustive analytical scheme having the required selectivity and sensitivity should be developed for the desorbed gases. Techniques such as infrared analysis, gas-liquid partition chromatography and mass spectrometry should be tried.

6. The possible interactions of active contaminants and decomposition of unstable contaminants should be investigated where critical to the analytical problem.

(s) Richard J. Grant

(s) Stanton B. Smith

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## TABLE I

## TYPICAL ANALYSIS OF INDUSTRIAL AIR POLLUTANTS

(Louisville, Kentucky)

| Component | Amount Present Mol. % of total pollutants collected |
|---|---|
| **Light Gases** | |
| Acetylene | .6 - 15 |
| n-Butane | 0 - 4 |
| Others | Traces |
| **Aromatics** | |
| Benzene | .2 - 3 |
| Toluene | Trace - 3 |
| Xylene and ethylbenzene | 0 - 1 |
| $C_{8}^{+}$ hydrocarbon | 0 - 1 |
| **Alcohols** | |
| Ethyl Alcohol | .3 - 3 |
| Others | Traces |
| Normal Traffic Gas | 30 - 75 |
| Oxidized Traffic Gas (Ref.) | 10 - 53 |
| Gasoline Vapor | Up to 50 |
| Approximate total pollutants in atmosphere | .2 - 1 ppm. |

(Approximated from Table 8, E. R. Weaver et al, NBS Journal of Research 59, 400 (57)

## TABLE II

### CRITICAL TEMPERATURE OF VARIOUS SUBSTANCES

(In Order of Increasing Critical Temp.)

| Substance | $T_c$, °C. | Substance | $T_c$, °C. |
|---|---|---|---|
| $N_2$ | -147 | $CH_3-CH-CH_3$ | 96.8 |
| CO | -140 | $H_2S$ | 100.4 |
| A | -122 | COS | 105 |
| $O_2$ | -118 | $CCl_2F_2$ | 111.5 (Freon 12) |
| NO | - 93 | $CH_2=C=CH_2$ | 120 |
| $CH_4$ | - 82.1 | $(CH_3)_2O$ | 126.9 |
| Kr | - 63.8 | $CH_3C\equiv CH$ | 128 |
| $BF_3$ | - 12.3 | $(CN)_2$ | 128 |
| $O_3$ | - 5 | Iso Butane | 134.9 |
| $CH_2=CH_2$ | + 9.2 | $H_2Se$ | 138 |
| Xe | 16.6 | $CH_3Cl$ | 143.1 |
| $CO_2$ | 31.1 | $Cl_2$ | 144 |
| $C_2H_6$ | 32.3 | HI | 150 |
| $CH\equiv CH$ | 35.5 | n-Butane | 152 |
| $N_2O$ | 36.5 | $SO_2$ | 157 |
| $CH_3F$ | 44.6 | $NO_2$ | 158 |
| $PH_4Cl$ | 49.1 | $(CH_3)_3N$ | 160 |
| $PH_3$ | 51.3 | $(CH_3)_4C$ | 160.6 |
| HCl | 51.4 | $(CH_3)_2NH$ | 164.5 |
| HBr | 90 | $C_2H_5OCH_3$ | 164.7 |
| $CH_3-CH=CH_2$ | 91.8 | $C_2H_5NH_2$ | 183 |
| $CHClF_2$ | 96.4 | HCN | 183.5 |
| | | $H_2O$ | 374.2 |

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## TABLE III

## PHYSICAL PROPERTIES OF ACTIVATED CARBONS

| | Burrell High Activity Charcoal (FB-11) | P.C.&C. Type BPL (S.S. No. 2) | P.C.&C. Type HDL (S.S. 5-2-58) |
|---|---|---|---|
| Particle Size (U. S. Sieve) | 35 x 60 | 4 x 10 | 6 x 16 |
| Bulk Density, g/cc. | .464 | .481 | .556 |
| Particle Density, g./cc. (by Hg Displacement) | | .806* | .889 |
| Real Density, g./cc. (by He Displacement) | | 2.10* | 2.146 |
| Carbon Tetrachloride Capacity, % (g. ads'd./100 g. carbon) | | 64.2 | 49.3 |
| Molasses Number | 172 | 195 | 174 |
| Iodine Number | 1300 | 1091 | 845 |
| Ash, % | 2.82 | 7.54 | 5.9 |

Note - Detailed analytical methods available on request from

PITTSBURGH COKE & CHEMICAL COMPANY
ACTIVATED CARBON DIVISION

* - (Determined on similar sample S.S. No. 1)

## TABLE IV

### PRELIMINARY RETENTION TESTS ON OVEN DRIED BPL ACTIVATED CARBON

**Adsorbent:** 5.7 g. BPL

| Temperature °C. | Carrier Gas | Gas Composition | Retention Volume, cc. at 25°C. |
|---|---|---|---|
| 25 | He | Methane | |
| | | $CH_4$ | 180 |
| | | Air (trace) | 65 |
| 25 | $N_2$ | Methane | |
| | | $CH_4$ | 150, 155 |
| 0 | $N_2$ | Coke Oven Gas | |
| | | $H_2$ | 15 |
| | | CO | 30, 35 |
| | | $CH_4$ | 260, 250 |
| 0 | $N_2$ | Methane | |
| | | $CH_4$ | 230, 225 |
| -78 | $N_2$ | Methane | |
| | | $CH_4$ | 1050, 850*, 1050 |

* Refrigerant level low

## TABLE V

### SPECIFIC RETENTION VOLUMES, cc./g.

1/4-inch Copper Tubes with 22 inches of Adsorbent

| Adsorbent | Weight, g. | 0°C. CO | 0°C. NO Peak 1 | 0°C. NO Peak 2* | 0°C. $CH_4$ | -78°C. CO | -78°C. NO Peak 1 | -78°C. NO Peak 2* | -78°C. $CH_4$ |
|---|---|---|---|---|---|---|---|---|---|
| BPL | 4.3 | - | - | - | 56 | - | - | - | 432 |
| HDL | 4.6 | 24 | 18 | 23 | 61 | 103 | 25 | 112 | 565 |
| | 3.1 | | | | | | | | 563 |
| HDL (dried) | 4.6 | 25 | 19 | 26 | 60 | - | - | - | 609 |
| Burrell Charcoal | 5.5 | - | - | - | 35 | - | - | - | 364 |
| $SiO_2$ | 3.7 | - | - | - | ** | - | - | - | 23 |
| Linde 5A | 7.6 | - | - | - | 18 | - | - | - | 74 |
| Linde 5A (dried) | 7.6 | - | 33 | 36 | 32 | - | - | - | 165 |

* Probably CO contamination

** No measurable retention at 0°C.

## TABLE VI

## RETENTION/BREAK VOLUMES

### 6 x 16 Mesh HDL Carbon, 3/4" O.D. Tube

| Run No. | Wt., g. | 200°C. React. Gas | Carrier Gas | Flow Rate | Column Temp. °C. | Test Gas | Influent Conc., ppm | Retention or Break Vol. liters | | Specific Retention or Break Vol. cc/g. | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 32.3g. | He | Air | 1 l./min. | -78°C. | $CH_4$ | 198 ppm cont. | 17-1/4 l. | (B) | 535 | (B) |
| 2 | 32.3g. | He | Air | 1 l./min. | -78°C. | $CH_4$ | 198 ppm cont. | 19 l. | (B) | 588 | (B) |
| 3 | 32.3 g. | He | He | 1 l./min. | -78°C. | $CH_4$ | 1,000 ppm inst. | >110 l. | (R) | - | |
| 4 | 55 g.* | He | Air | 1 l./min. | -78°C. | $CH_4$ | >3,000 ppm inst. | 31 l. | (R) | 565 | (R) |
| 5 | 55 g.* | Air | Air | 1 l./min. | -78°C. | $CH_4$ | 120 ppm cont. | 12 l. | (B) | 218 | (B) |
| 6 | 55 g. | Air | Air | 1 l./min. | -78°C. | $CH_4$ | >3,000 ppm inst. | 31 l. | (R) | 565 | (R) |
| 7 | 55 g. | Air | Air | 1 l./min. | -78°C. | $CH_4$ | 144 ppm cont. | 24 l. | (B) | 436 | (B) |
| 8 | 55 g. | He | Air | 1 l./min. | -78°C. | $CH_4$ | 156 ppm cont. | 31 l. | (B) | 565 | (B) |
| 9 | 55 g. | He | He | 100 cc./min. | 200°C. | $CH_4$ | 1,000 ppm inst. | 0.225 l. | (R) | 4.1 | (R) |
| 10 | 55 g. | He | He | 100 cc./min. | 200°C. | $C_2H_4$ | 1,000 ppm inst. | 0.500 l. | (R) | 9.1 | (R) |
| 11 | 55 g. | He | He | 100 cc./min. | 200°C. | $C_3H_8$ | 1,000 ppm inst. | 2.9 l. | (R) | 52.8 | (R) |
| | | | | | | | **35 x 60 Mesh HDL Carbon, 6 mm. O.D. Tube** | | | | |
| 12 | 1.5 g. | He | Air | 1 l./min. | 25°C. | $C_4H_{10}$ | 100 ppm cont. | 150 l. | (B) | 100,000 | (B) |

* One-Inch O.D. Collector

## TABLE VII

## EFFICIENCY OF RECOVERY

Adsorbent: 6 x 16 Mesh HDL Activated Carbon - Tube O.D.: 3/4" - Adsorption Temp.: -78°C. - Desorption Temp.: 200°C.

| Run No. | wt. Carbon | Gas | Conc'n. in Air | Carrier Gas Flow Rate | Vol. Air Sampled | Total Gas Vol., cc. | Sampling Pressure psig. | Vol. -78° He Flush | Desorption Flow Rate, He | IR Peak Ht.* Adsorbance Units | % Recovery |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Reference | $CH_4$ | - | 100 cc./min. | - | 1 | 5 | - | - | 0.131 | |
| | Reference | $CH_4$ | - | 100 cc./min. | - | 1 | 5 | - | - | 0.142, 0.139 | |
| | Reference | $CH_4$ | - | 50 cc./min. | - | 1 | 5 | - | - | 0.112 | |
| 13 | 32.3 g. | $CH_4$ | 120 ppm | 1 l./min. | 10 l. | 1 | 3 | 9-1/2 l. | 60 cc./min. | 0.105 | 93% |
| 14 | 55 g. | $CH_4$ | 120 ppm | 1 l./min. | 20 l. | 2 | 3 | 9 l. | 50 cc./min. | 0.217 | 97% |
| | Reference | $C_2H_4$ | - | 70 cc./min. | - | 1 | 5 | - | - | 0.271 | |
| | Reference | $C_2H_4$ | - | 55 cc./min. | - | 2 | 5 | - | - | 0.477 | |
| 15 | 55 g. | $C_2H_4$ | 120 ppm | 1 l./min. | 20 l. | 2 | 3 | 15 l. | 100 cc./min. | 0.430 | 90% |
| | Reference | $C_3H_8$ | - | 50 cc./min. | - | 1 | 5 | - | - | 0.300 | |
| | Reference | $C_3H_8$ | - | 50 cc./min. | - | 2 | 5 | - | - | 0.70 | |
| 16 | 55 g. | $C_3H_8$ | 120 ppm | 1 l./min. | 20 l. | 2 | 3 | 15 l. | 100 cc./min.** | 0.71 | 100% |
| | Adsorbent: | 35 x 60 Mesh HDL Carbon | | - Tube O.D.: 6 mm. - Adsorption Temp.: 25°C. - Desorption Temp.: 200°C. | | | | | | | |
| | Reference | $C_6H_6$ | 102 ppm | 100 cc./min. | 1 l. | 0.102 cc. | - | - | - | 0.043-.032# = .011 | |
| | Reference | $C_6H_6$ | 463 ppm | 100 cc./min. | 1 l. | 0.463 cc. | - | - | - | 0.106-.032# = .074 | |
| | Reference | $C_6H_6$ | 463 ppm | 100 cc./min. | 1 l. | 0.463 cc. | - | - | - | 0.102-.032# = .070 | |
| 17 | 1.5 g. | $C_6H_6$ | 77.5 ppm | 1 l./min. | 20 l. | 1.55 cc. | - | - | - | .196-.040# = .156 | 61% |

* Analytical Wavelengths Used: $CH_4$ - 7.65 μ; $C_2H_4$ - 10.5 μ; $C_3H_8$ - 3.3 μ; $C_6H_6$ - 14.6 μ
** Reverse Flush
# Base Line Correction

FIGURE 1a

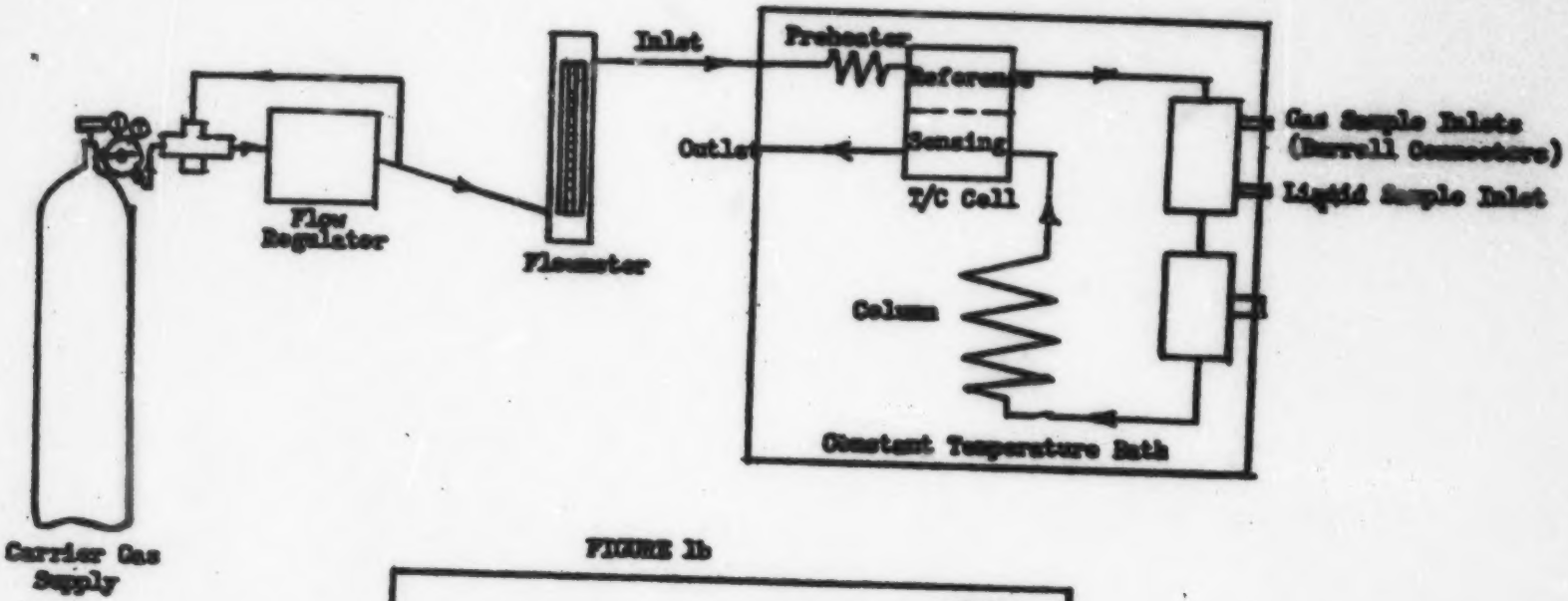
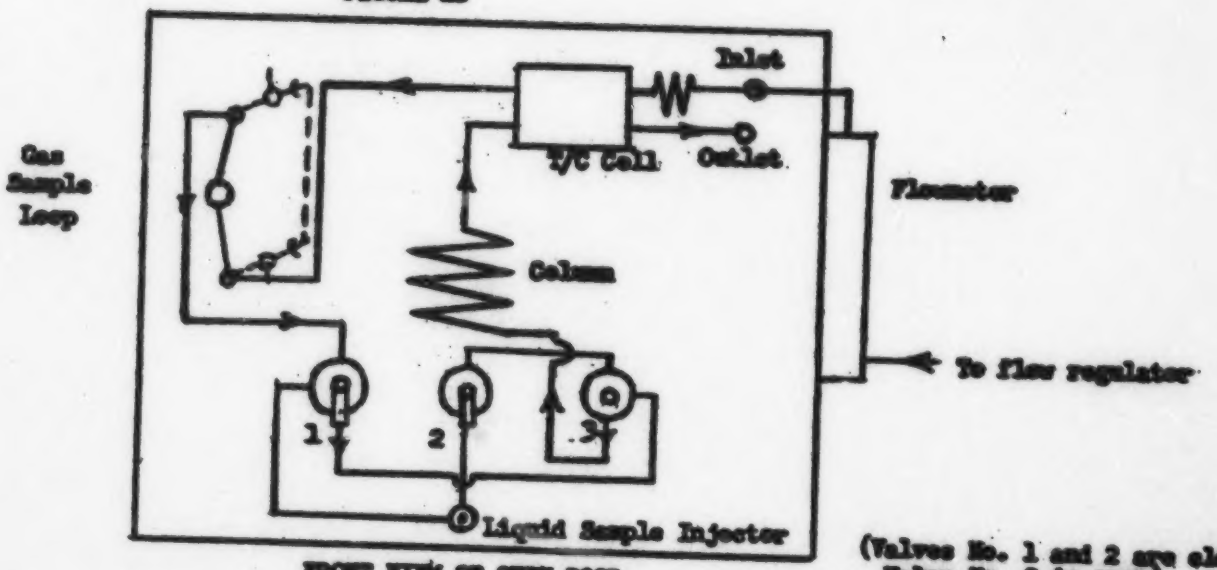



FIGURE 1b




FRONT VIEW OF OVEN DOOR

(Valves No. 1 and 2 are closed. Valve No. 3 is open)

Valves are in this position for gas samples

FIGURE 2

BRIDGE CIRCUIT

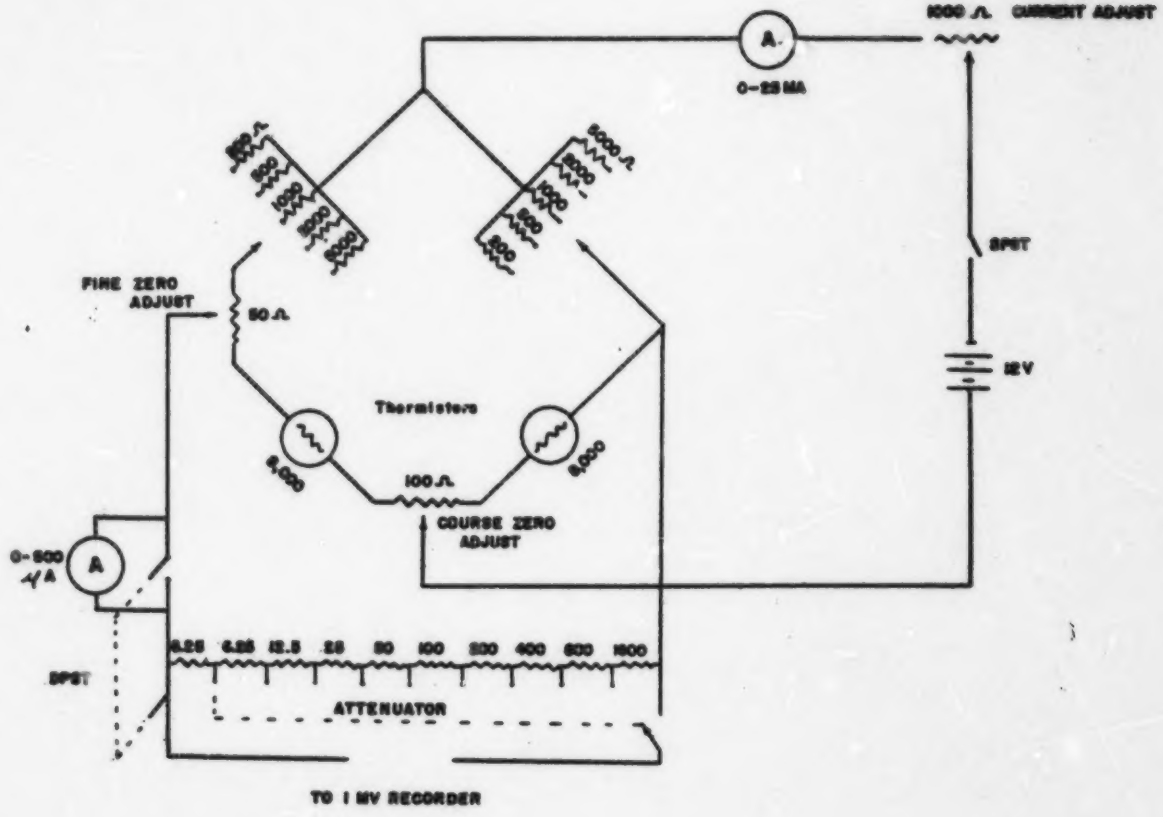
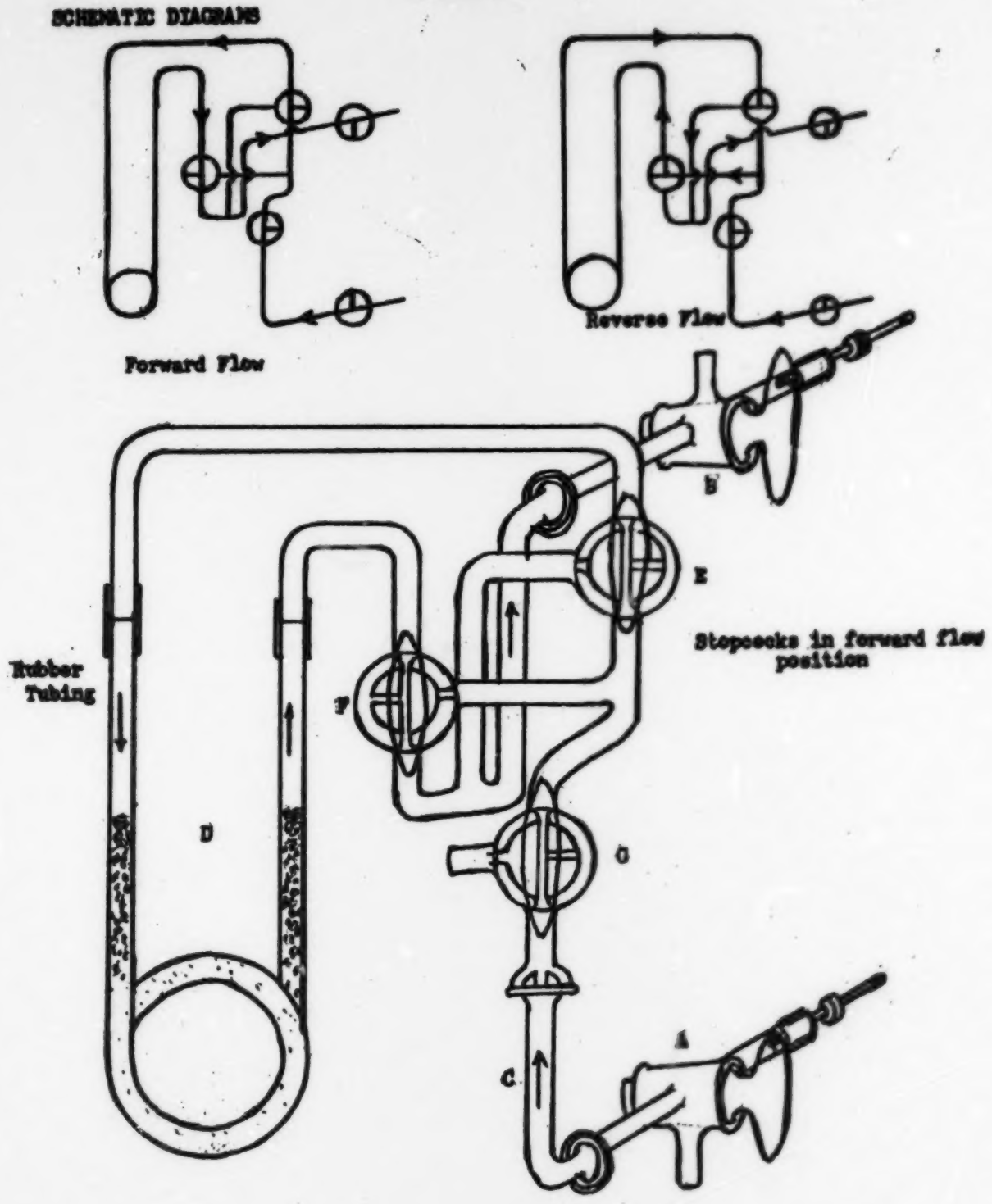


FIGURE 3




REVERSIBLE FLOW COLUMN

FIGURE 4

PORE SIZE DISTRIBUTION
PITTSBURGH GRANULAR GAS-PHASE CARBON

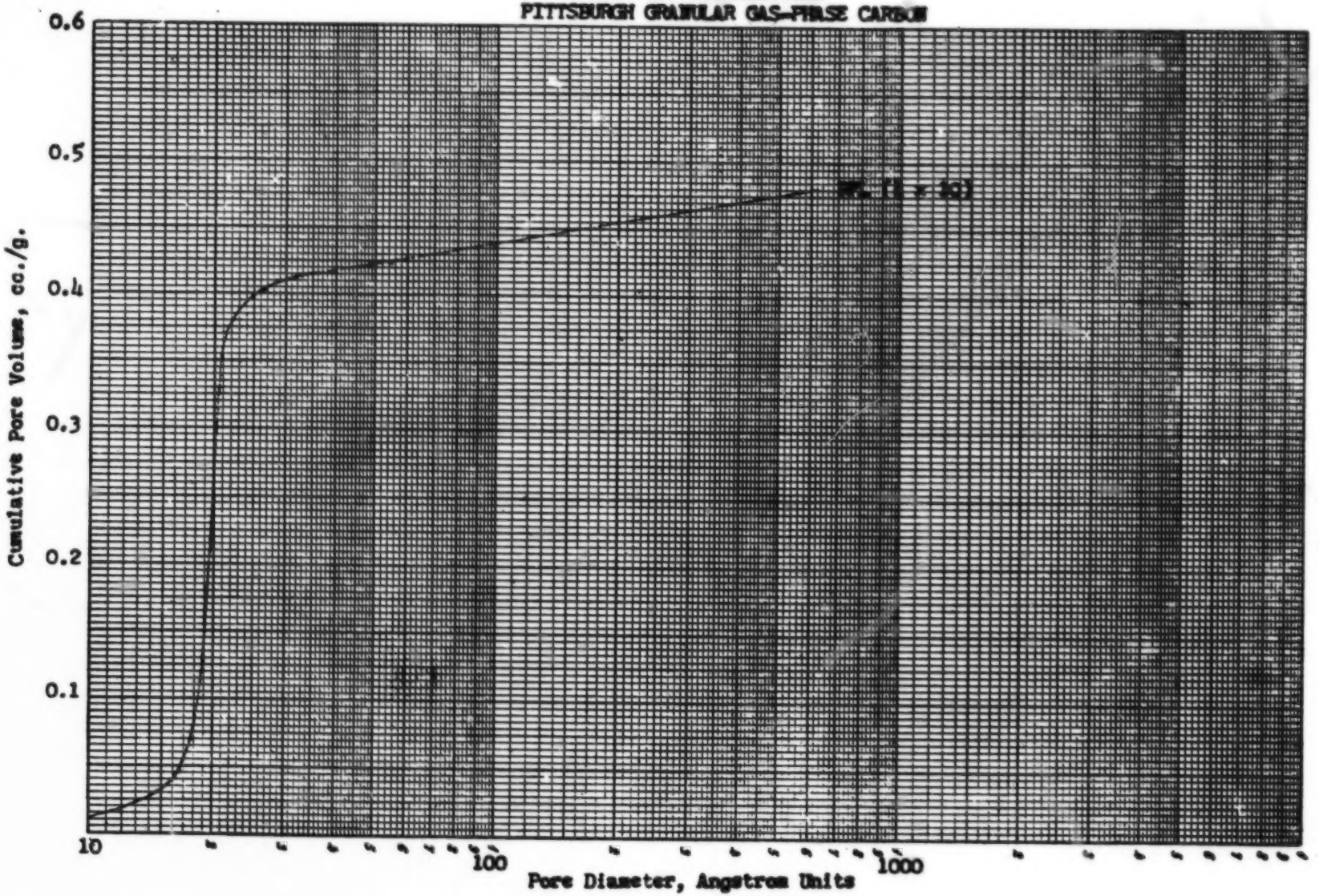


FIGURE 5
PORE SIZE DISTRIBUTION

PITTSBURGH GRANULAR GAS-PHASE CARBON
HDL (6X16) SAMPLE STOCK 5-2-58

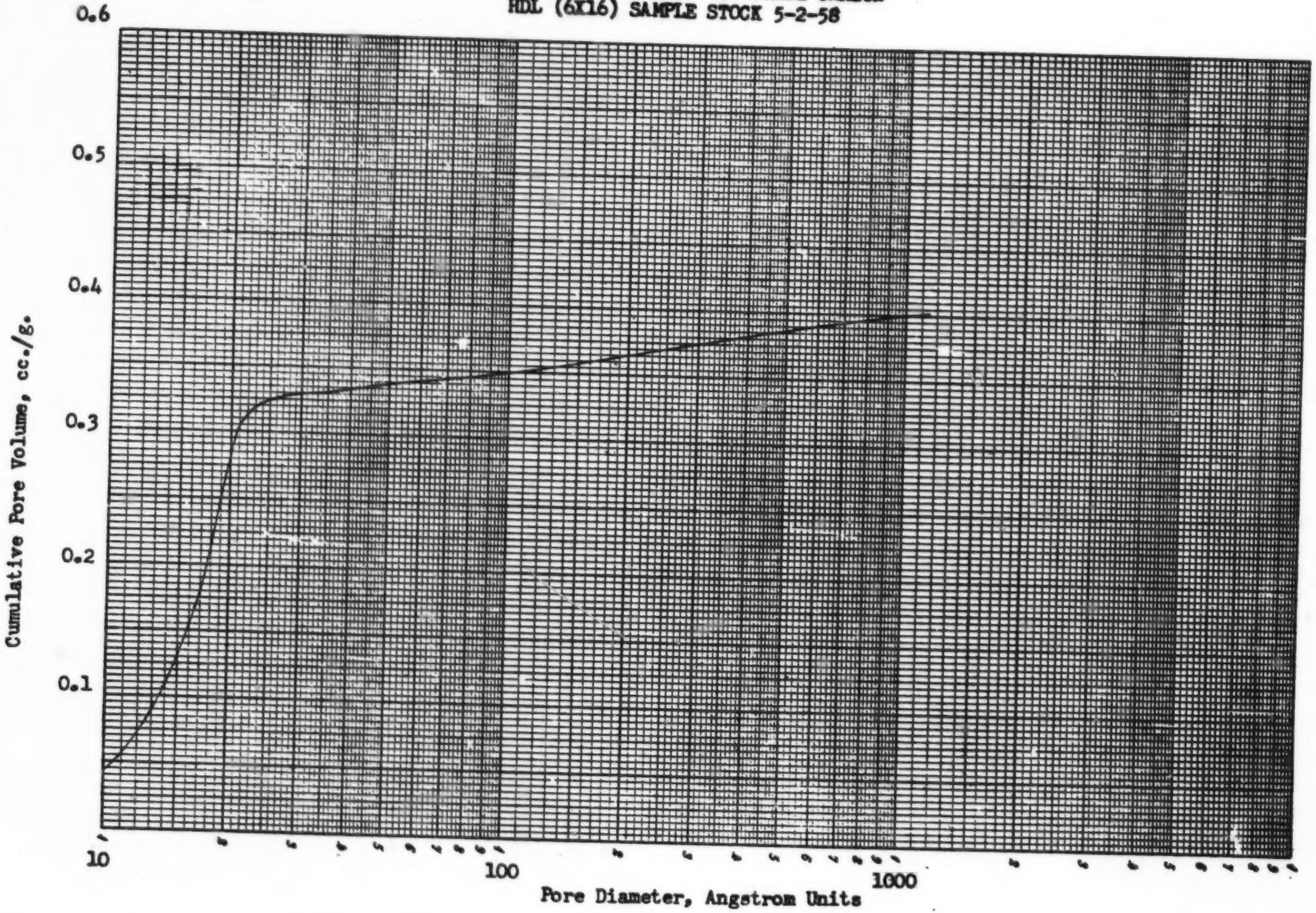


FIGURE 6
PORE SIZE DISTRIBUTION

FB-11 (CHARCOAL-KROMO-TOG)

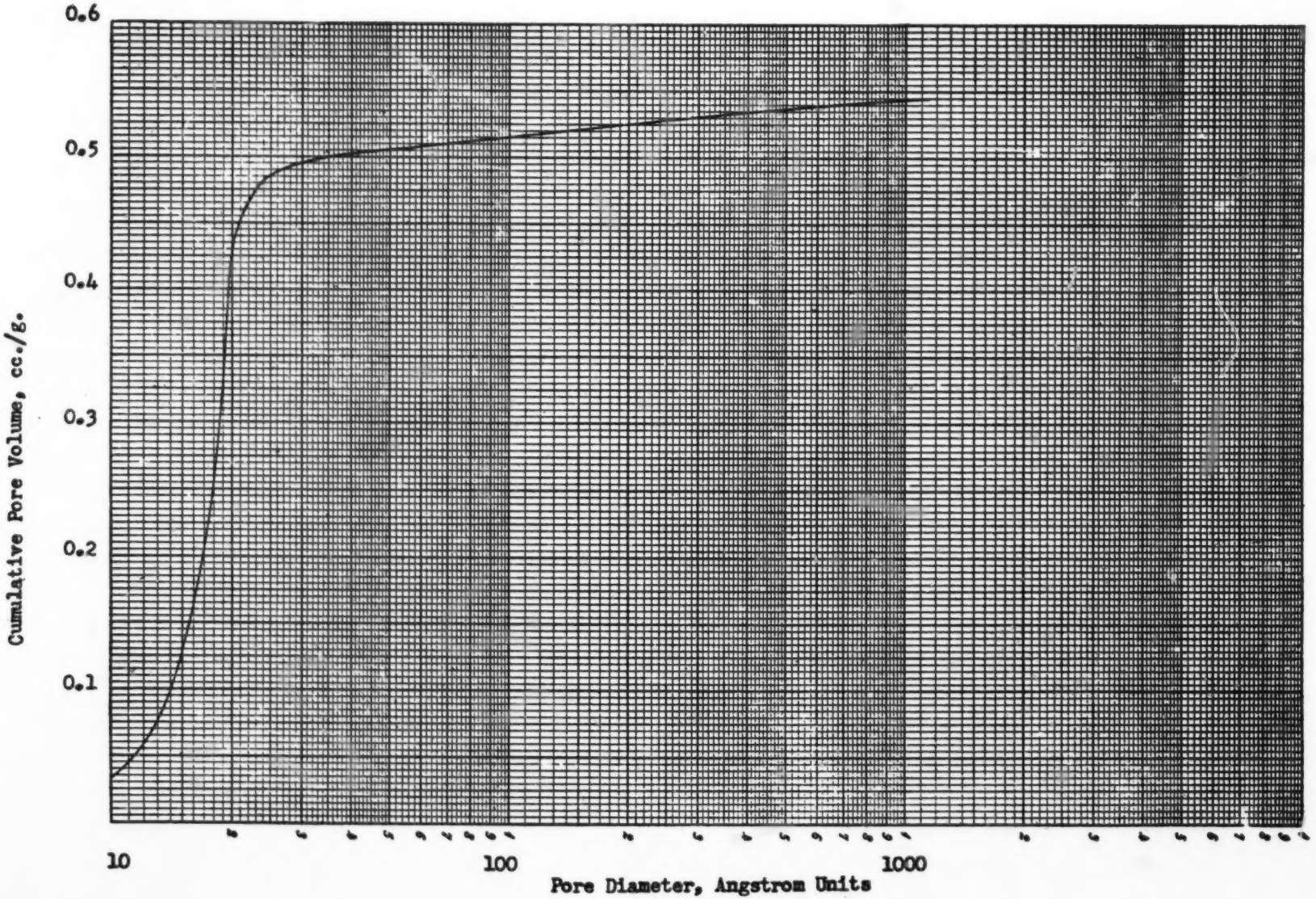
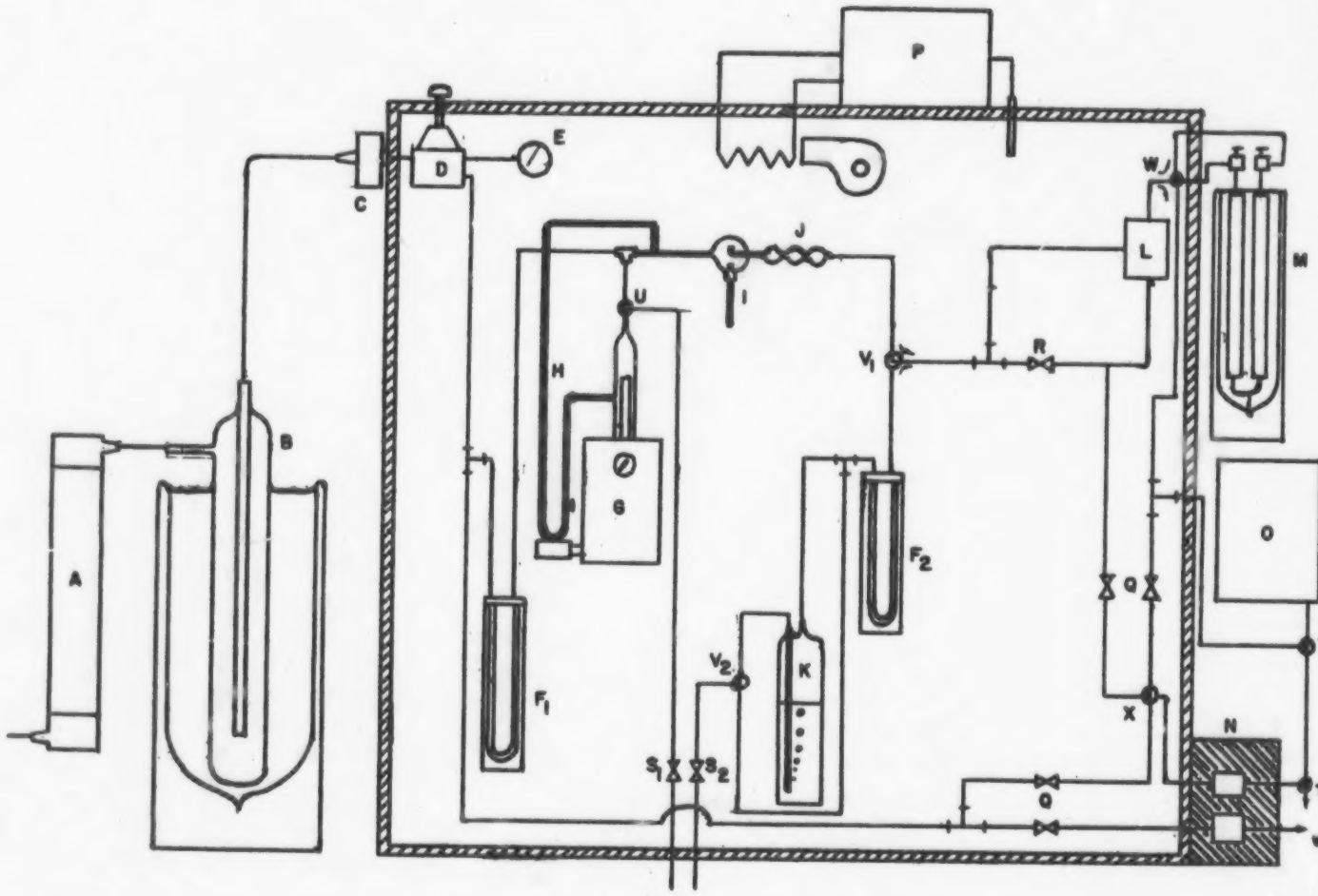


FIGURE 7

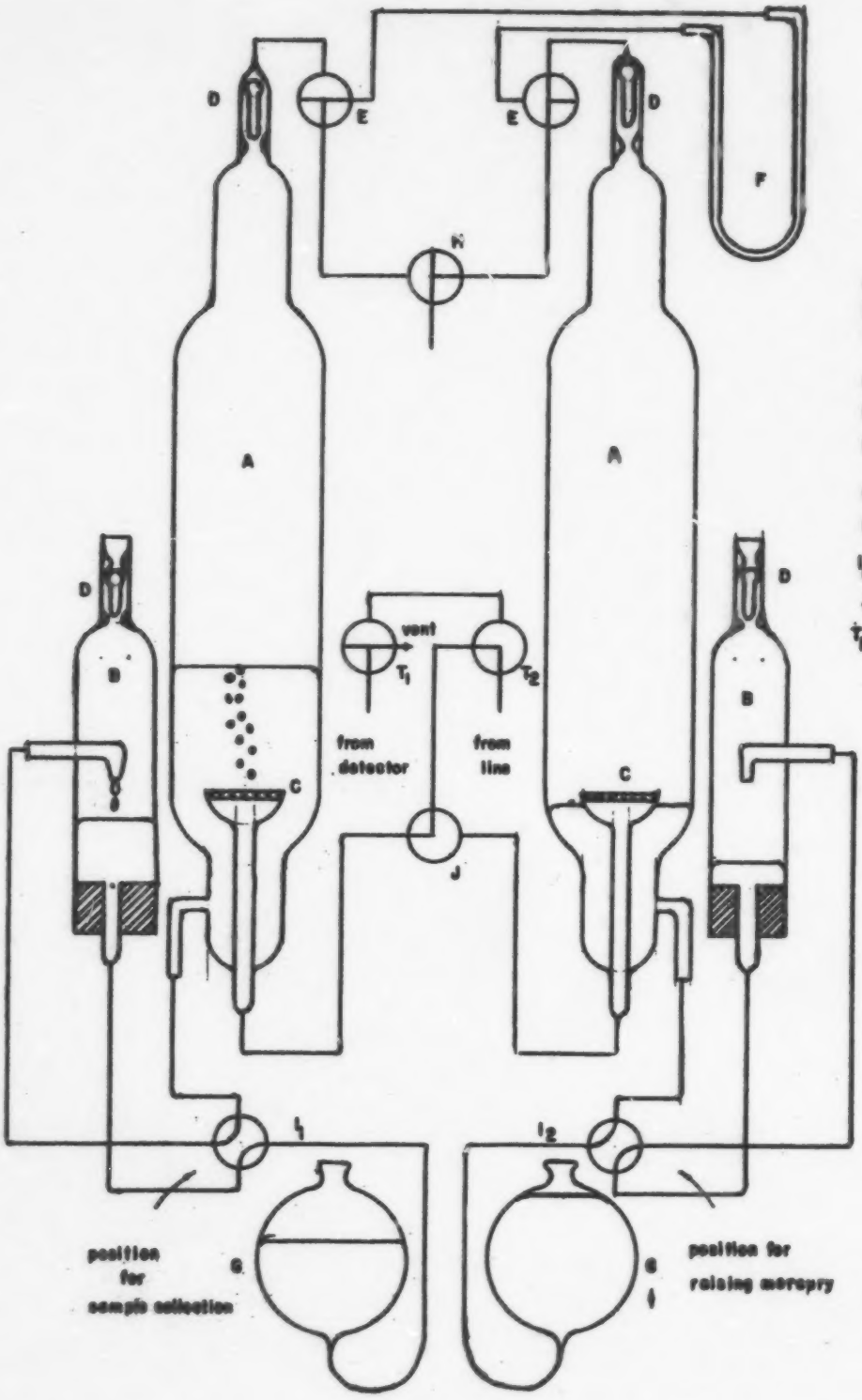
COLLECTOR EFFICIENCY TEST LINE




A - Drierite Tower
B - Activated Carbon trap
C - Aerosol filter
D - Pressure regulator
E - Pressure gauge
$F_1$ $F_2$ - Capillary flowmeters
G - Meniscomatic buret
H - Null manometer
I - Diffusion cell
J - Mixer
K - Displacer saturator
L - Differential flow controller
M - Sample collector
N - Detector cell
O - Collection Devices
P - Bath-temperature controller
Q - Detector flow control needle valves
R - Main flow control needle valve
$S_1$ $S_2$ - Gas supply shut-off valve
$T_1$ $T_2$ - Collection cocks
U - Syringe filling cock
$V_1$ $V_2$ - Displacer flow switching cocks
W - Collector by-pass cock
X - Detector selector cock

FIGURE 8

GAS SAMPLE COLLECTION DEVICES




A - Toeppler pump collector
B - Overflow device
C - Submerged fritted glass disc
D - Glass float valves
E - Three-way cocks, S.S.
F - Trap, GLC column or IR cell
G - Hg leveling bulbs
H - Vacuum cock, S.S.
$I_1$ $I_2$ - Four-way cocks, S.S.
J - Two-way cock, S.S.
$T_1$ $T_2$ - Collection cocks

FIGURE 9

PROTOTYPE COLLECTOR SYSTEM

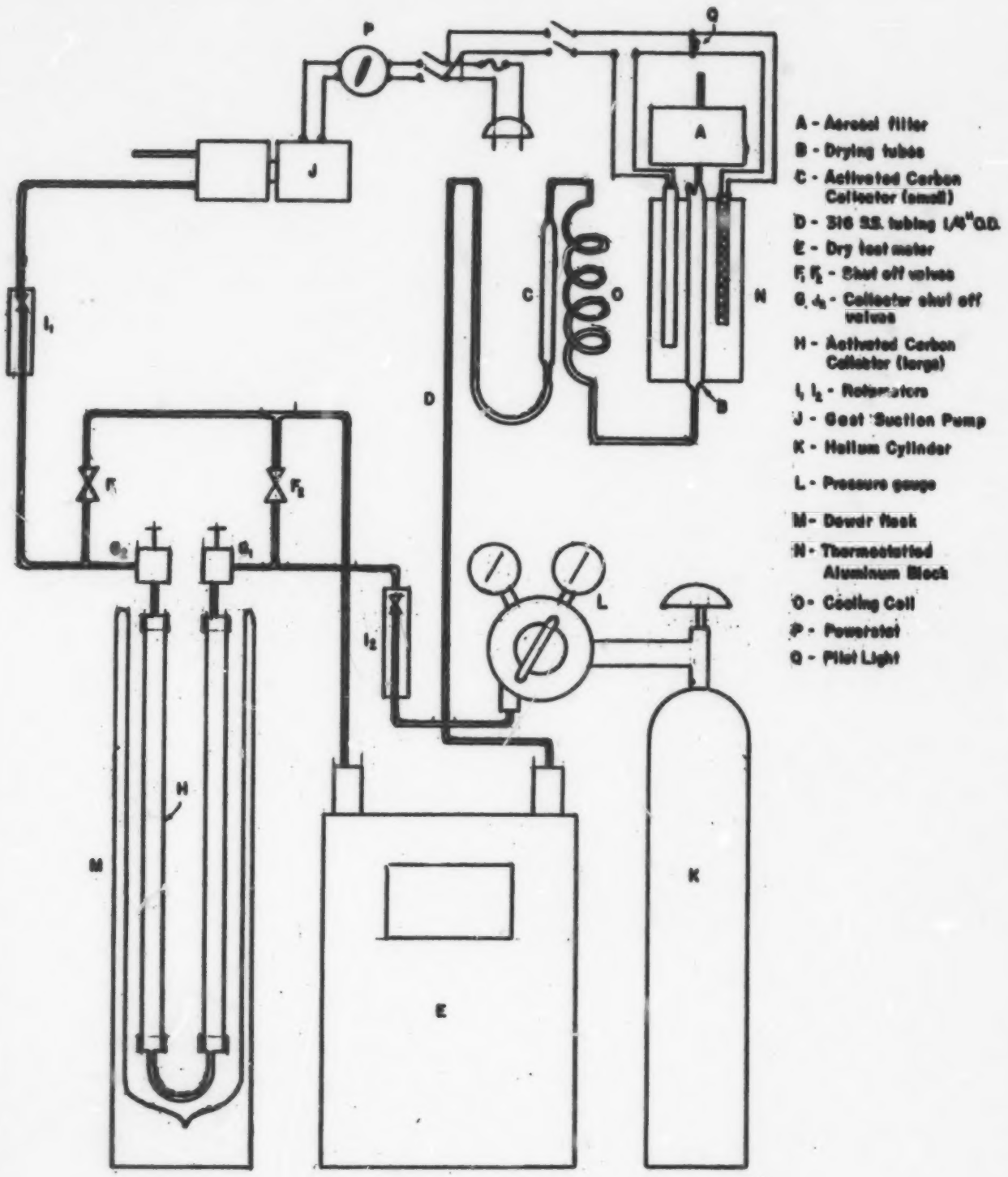
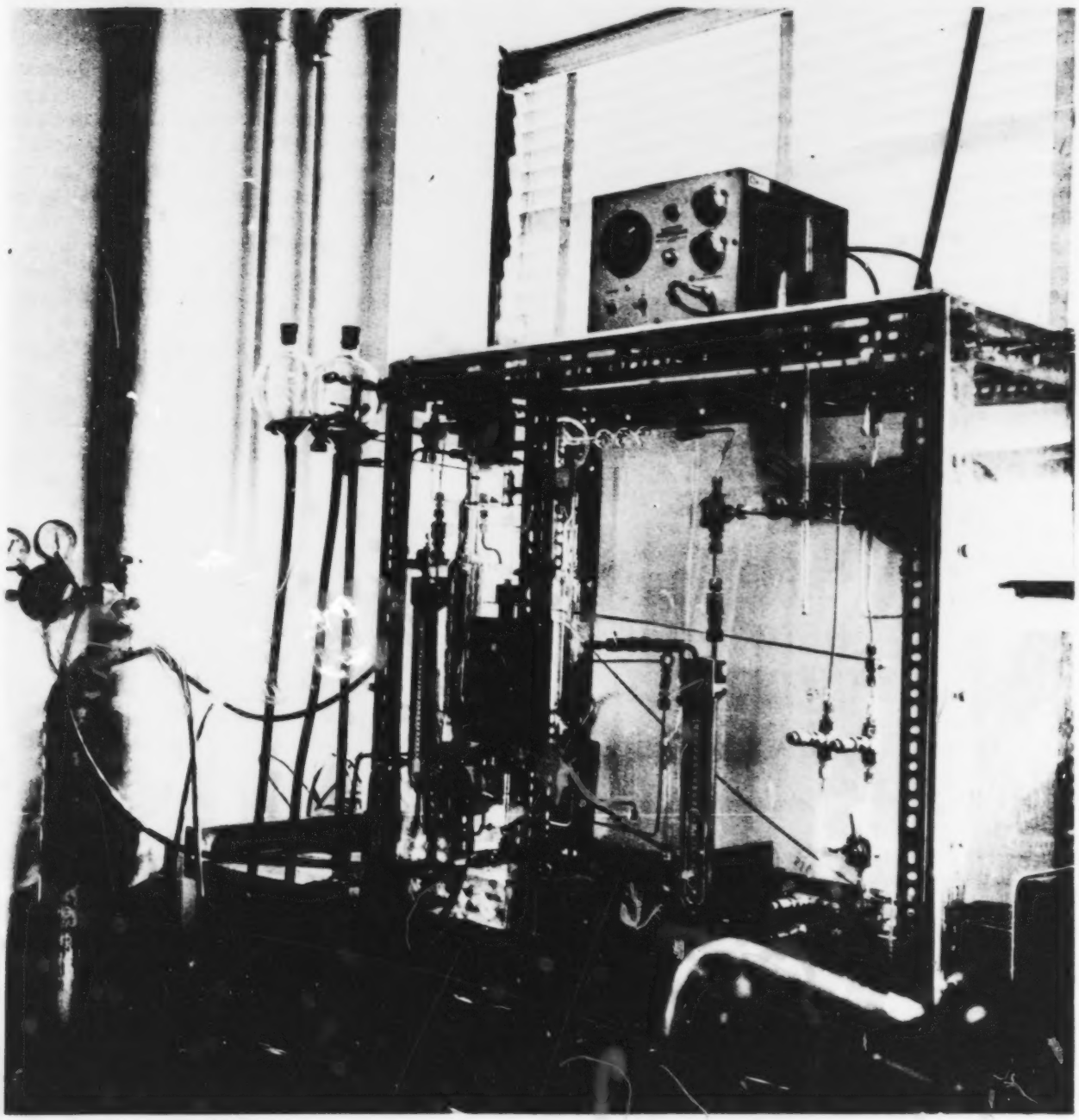


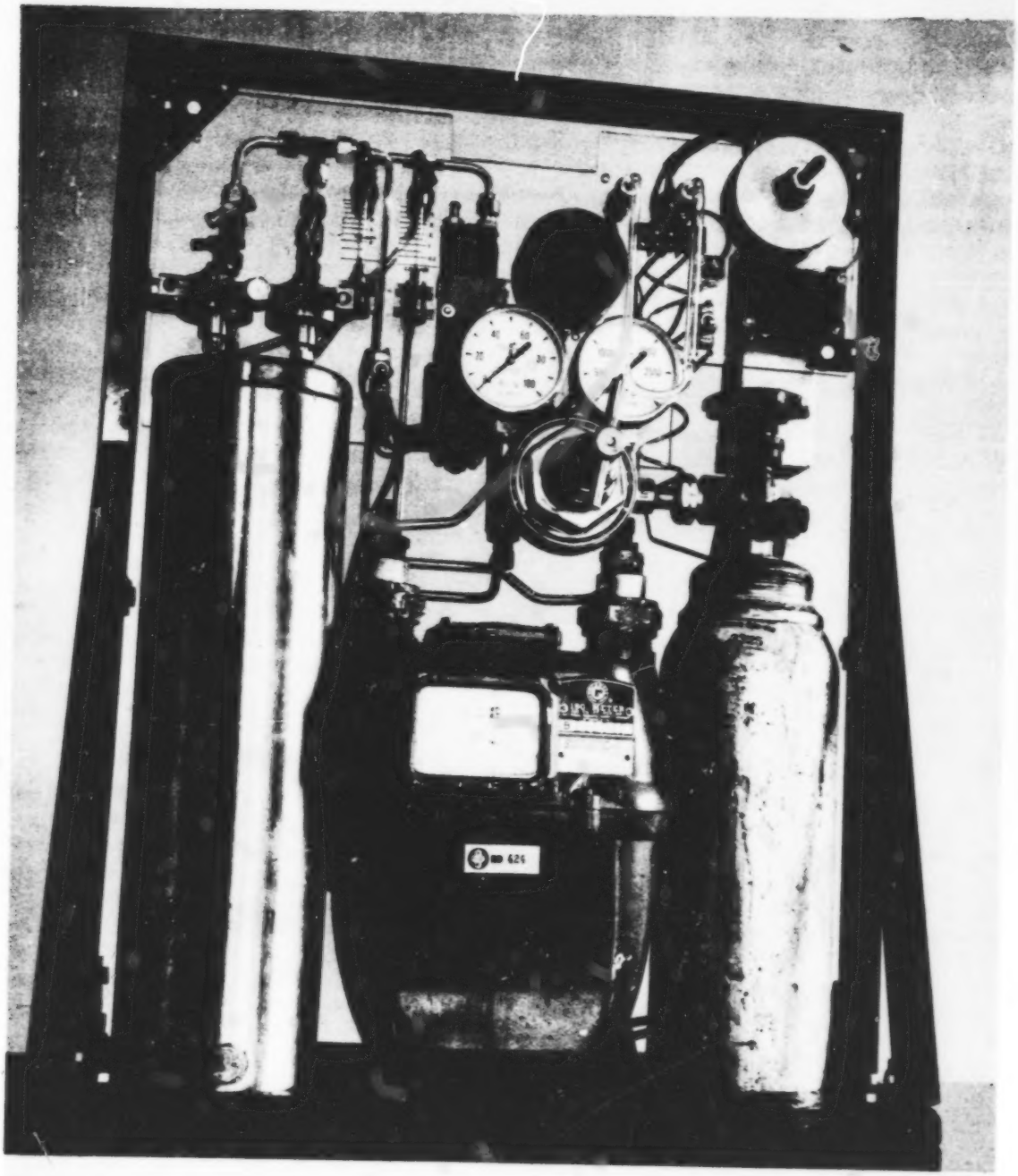
PLATE I



COLLECTOR EFFICIENCY TEST APPARATUS

(See Flow Diagrams, Figures 7 & 8)

PLATE II



GASEOUS AIR POLLUTANT COLLECTOR FIELD KIT

Front View

(SEE FLOW DIAGRAM, FIGURE 9)

KEY TO PLATE II

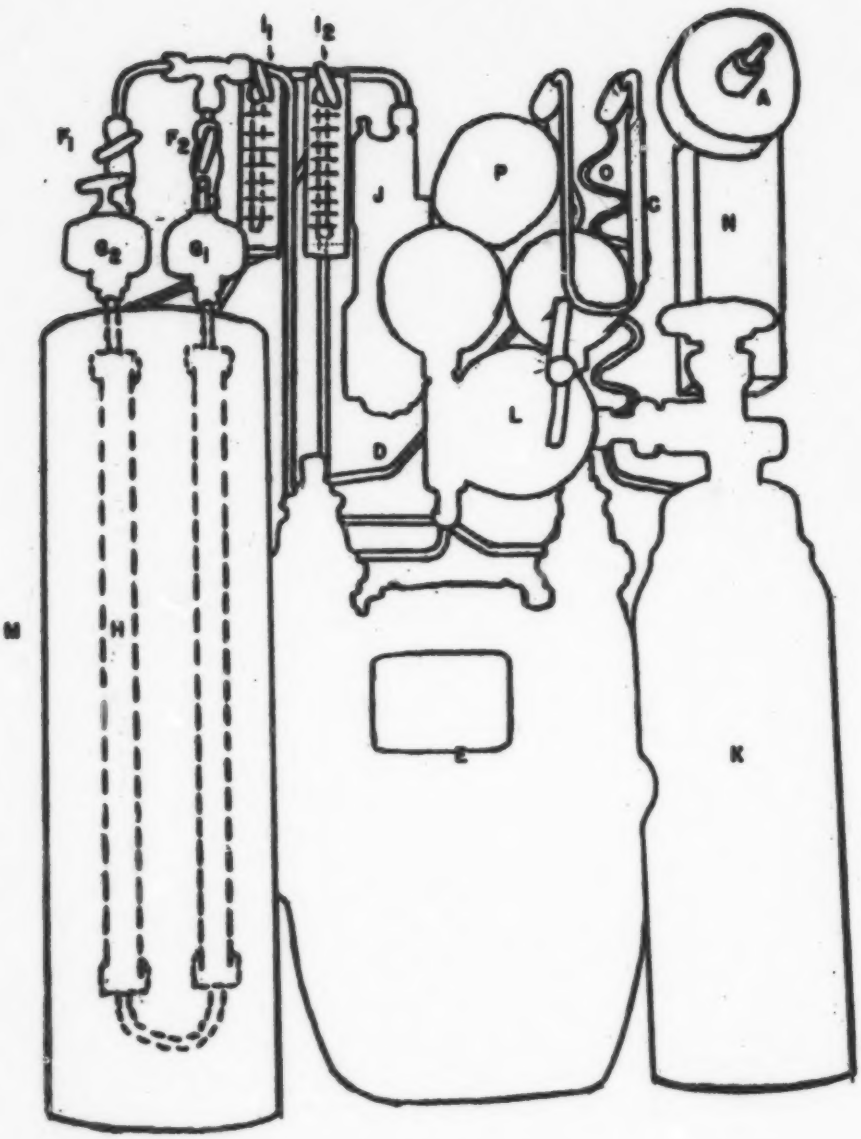
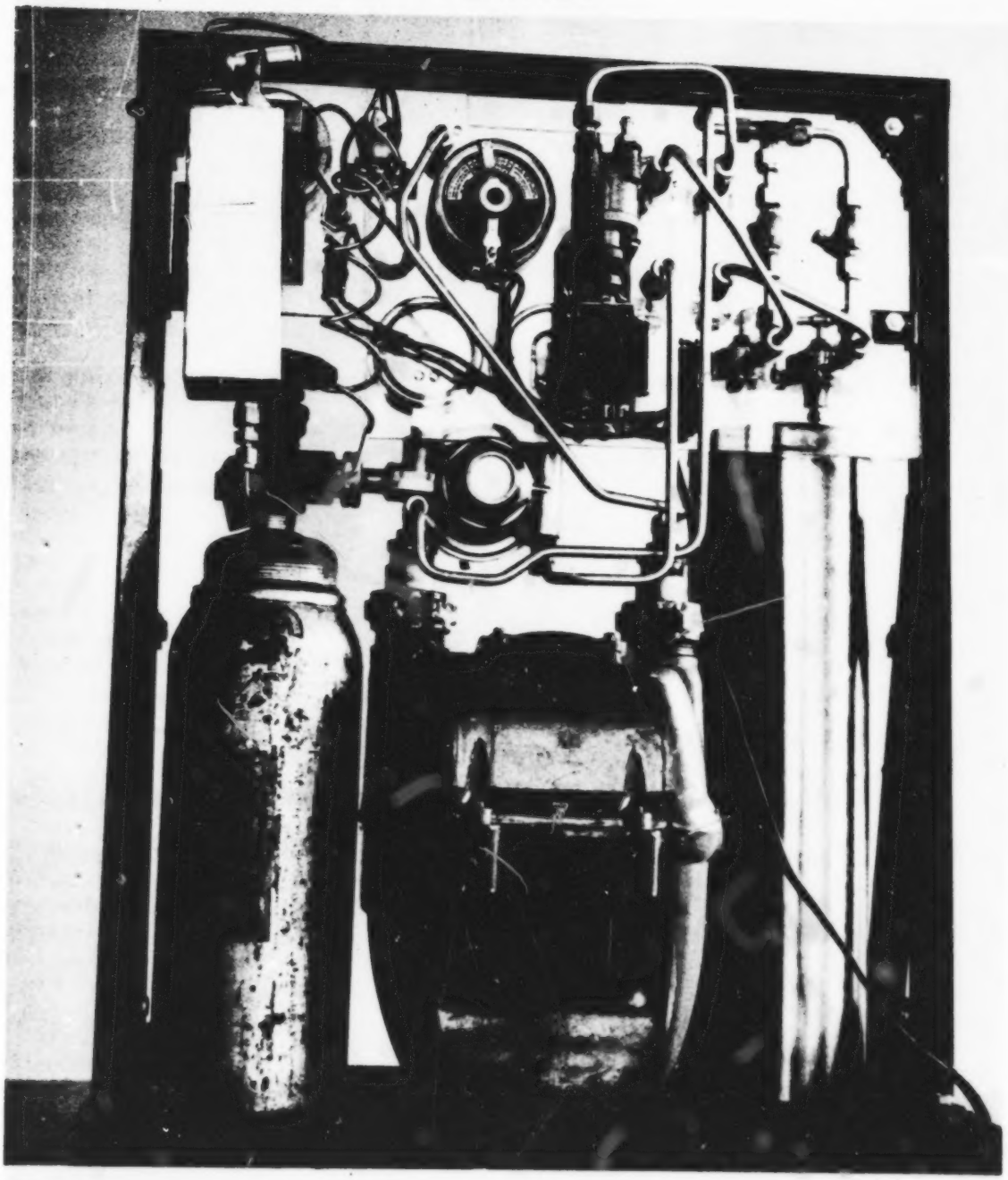


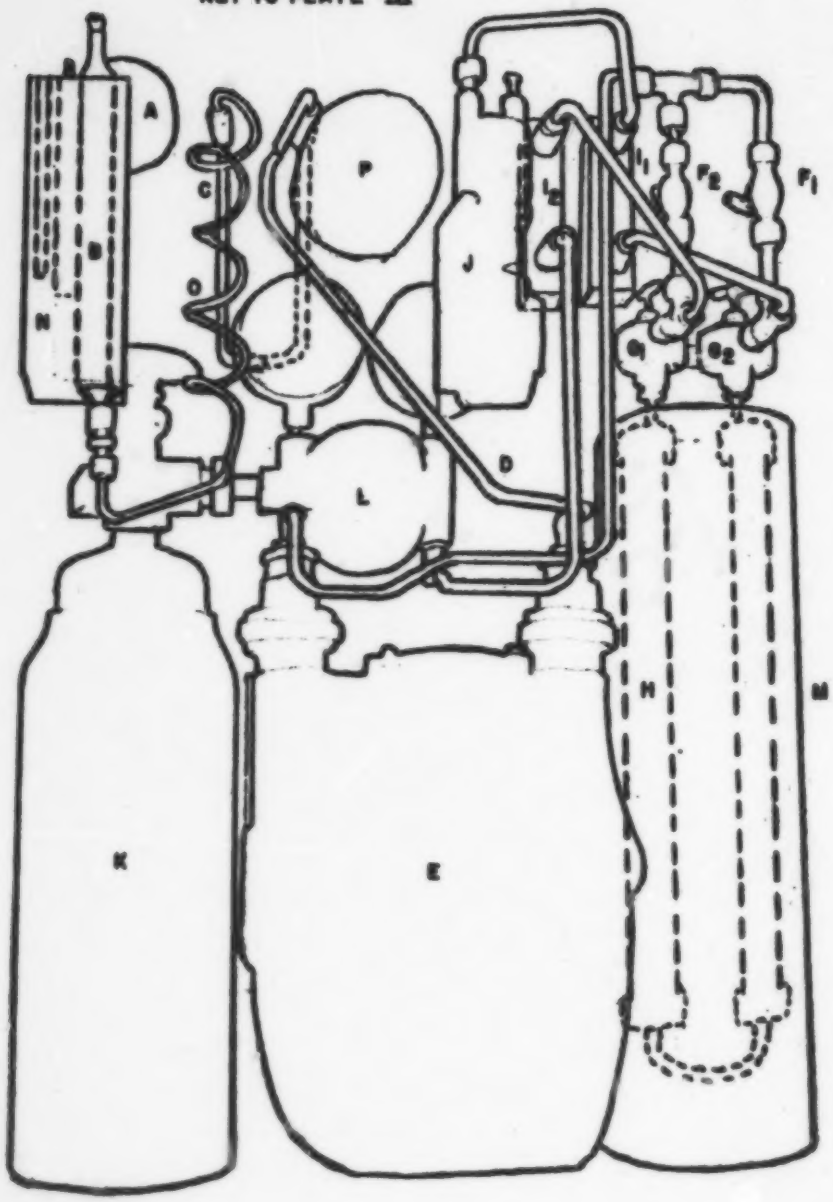
PLATE III



GASEOUS AIR POLLUTANT COLLECTOR FIELD KIT
Rear View

(SEE FLOW DIAGRAM, FIGURE 9)

KEY TO PLATE III



# APPENDICES

A - B - C - D

## APPENDIX A

## SPECIAL CONTRACT PROVISIONS OF CONTRACT NO. SAPH-68345

**PURPOSE:** A Non-Selective Collector for Sampling Gaseous Air Pollutants

**ARTICLE 1. - Scope of Work and Services**

The Contractor shall, as an independent contractor, exert its best efforts to conduct studies and investigations of, and supply the necessary personnel, labor, supplies, services, and facilities and do all other things necessary for and incident to the performance of this contract, the adsorption of various gases and vapors known to be pollutants in smog atmospheres on columns of activated carbons of various types over a range of concentrations. The objective of this investigation is the design of an efficient non-selective collector for gaseous air-borne contaminants. Desorption of the various agents will be attempted by thermal or displacement methods, and the degree of recovery estimated by infrared spectroscopy, gas chromatography or other techniques.

Chemical interactions in the adsorbed phase may be briefly investigated on selected pairs of gases and possibly on more complex mixtures if time permits. The investigation should result in the selection of the proper adsorbent, or adsorbents, to be used in a column of designated size under a preferred set of conditions which will result in a known degree of recovery of certain classes of pollutants. When this column or canister is desorbed under the prescribed conditions, a known recovery of the above classes of compounds should be obtained, and the resulting quantity of gas used in further analysis.

**APPROACH**

The approach to the desired objectives will include as many of the following and other items as are necessary and feasible as developed with advice and consultation of the project officer.

1. Measurement of the adsorptive capacities (under equilibrium conditions) of selected activated carbons for typical pollutant gases over a range of low partial pressures (concentrations) at appropriate temperatures. Gases and vapors tested will be representative of the following classes: aliphatic and olefinic hydrocarbons ($C_1$ to $C_8$), aromatic hydrocarbons, aldehydes, ketones, alcohols, sulfur gases, and nitrogen oxides.

2. Conditions necessary for quantitative desorption without decomposition will be investigated for the various compounds. The application of heat and vacuum or the use of displacing agents will be attempted.

3. The extent of collection of trace quantities of various gases in air will be checked in a flow system, and the efficiency of recovery by desorption measured by means of infrared analyses and/or gas chromatography.

4. The most promising activated carbons or combination of carbon and other adsorbents will be selected and the most suitable canister dimensions and collection conditions recommended.

5. A suitable set of desorption conditions for satisfactory recovery of adsorbed vapors will be found and rated on pure components and typical mixtures of several components.

6. The possibility of interaction between strongly oxidising pollutant gases with organic components will be investigated; and if found to be serious, measures for avoiding this interference will be taken. For example, the reaction of $NO_2$ on unsaturated hydrocarbons on the carbon surface will be studied.

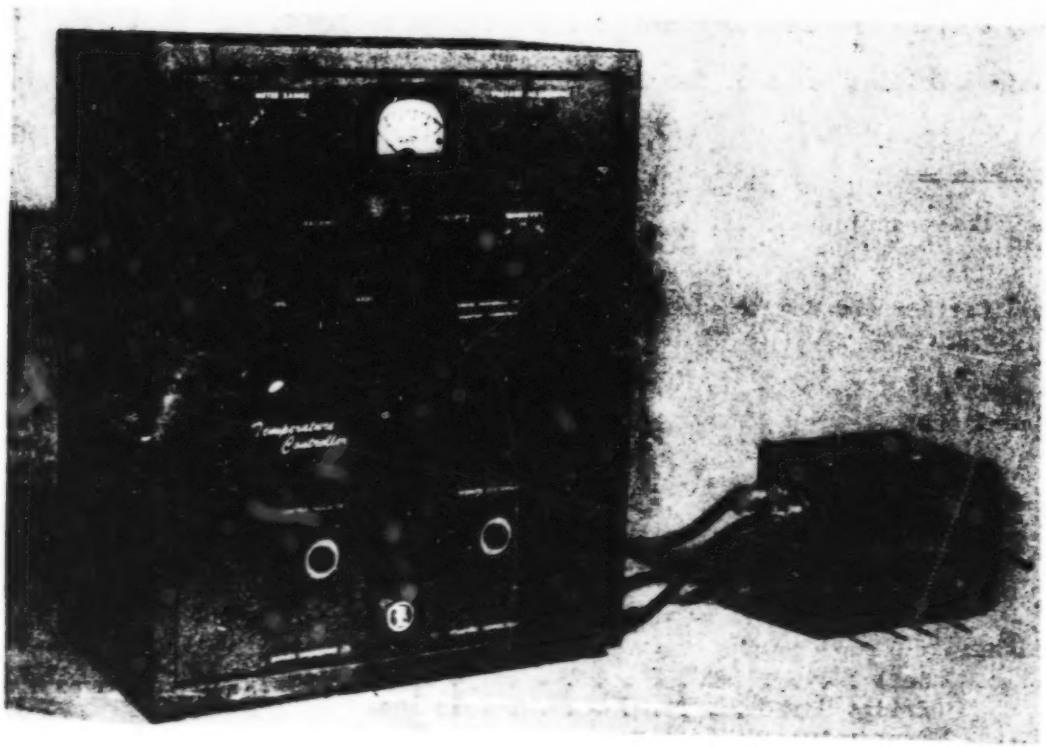
Barnes Engineering Company

*Infrared Components and Systems*
*Automation Equipment*
*Process Control Instrumentation*

38 Commerce Road, Stamford, Connecticut

THERMAL CONDUCTIVITY CELL MODEL 75

Thermistor Flake Detectors Extend Range of Vapor Chromatography
Cell Unit Precisely Controlled Over 30°C to 325°C Range
Measurement of Sample Fractions with Boiling Points Up to 425°C



SPECIFICATIONS

Model 75 Thermal Conductivity Cell includes: 1 temperature-controlled thermal conductivity cell, 1 bridge unit, 1 temperature controller unit, 2 connecting cables, 1 line cord. Bristol Dynamaster recorder available at extra cost, chromatographic column and associated accessories not supplied.

Performance

| | |
|---|---|
| Detector Type | Temperature Stabilized Flake Thermistors |
| Cell Response Speed | 0.25 second |
| Sensitivity | 1 part in 10,000,000 |
| Temperature Control Accuracy | $\pm$ .01°C. |
| Cell Temperature Control Range | 30°C. to 325°C. |
| Maximum Boiling Point of Samples | 425°C. |

Mechanical

| | |
|---|---|
| Cell Construction | Type 316 Stainless Steel Throughout |
| Cell Carrier and Sample Lines | 1/4" O.D. x 3 3/8" Lg. Type 316 Stainless Steel |

Dimensions:

| | |
|---|---|
| Cell | 7 1/8" W x 5 1/2" H x 5-1/8" Deep Plus 3 3/8"-Long Tube Lengths |
| Bridge Unit | 15 1/2" W x 9 1/2" H x 9 1/2" Deep |
| Temperature Controller | 15 1/2" W x 9 1/2" H x 9 1/2" Deep |

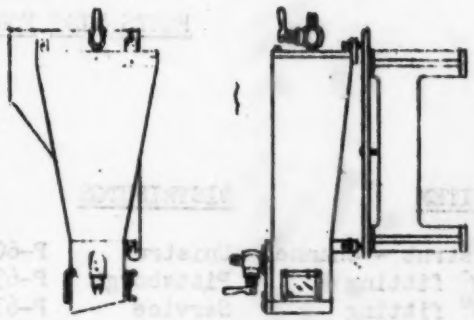
Weight:

| | |
|---|---|
| Cell | 4 1/4 lbs. |
| Bridge Unit | 13 lbs. |
| Temperature Controller | 15 1/2 lbs. |

| | |
|---|---|
| Power Requirements | 117 Volts, 60 cycles, Single Phase<br>*Maximum Power: 150 Watts*<br>Average Operating Power: 50 Watts |

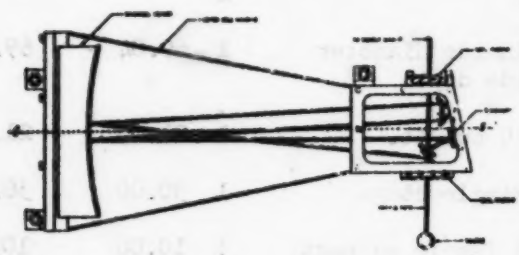
# 1 METER PATH LENGTH CELL

- For gas studies
- Advanced optical design
- For use with all Baird-Atomic Infrared Spectrophotometers
- Easily flushed between runs



The 1 meter path length cell is a gas sample cell designed for analytical use in all Baird-Atomic infrared spectrophotometers. The location of the cell is identical in the 4-55 and KM-1 instruments, currently in production, as well as the earlier A B models.

The cell provides a 1 meter path length, obtained by 4 traversals of the beam in the interior of the cell (note drawing of optical path). The entrance end of the cell, that placed in the sample beam, contains an entrance window, an exit window and 5 reflecting surfaces. The latter are all flat, first surface aluminized mirrors. A concave mirror is positioned at the opposite end of the cell. The optical design allows for 7 reflections of the beam and provides several advantages. Minimum vignetting and distortion of the beam is chieved by the one-to-one imaging system of the concave mirror and the inside corner reflections of the 3rd and 4th mirrors.



The cell body is stainless steel. Entrance and exit valve connections are placed at either end to reduce entrapment of gases when flushing. The cell may be evacuated or will withstand a pressure of 15 psig.

The cell intercepts the sample beam between the globar and the sample beam cross mirror. The cell body occupies a space between the sample and reference beams. A kinematic mounting supports the cell and provides for accurate and rapid positioning of the unit. Filling of the cell may be accomplished with the spectrophotometer cover in place or removed, at the discretion of the operator.

The cell has a volume of approximately 1,000 cc.

Path length tolerance is ± 1%

Price . . . . . [redacted] f.o.b. Cambridge, Massachusetts

Bulletin IR-449

BAIRD ATOMIC

*Baird-Atomic, Inc.*

33 University Road, Cambridge 38, Massachusetts

PRINTED IN U.S.A.

1M-7-57 BB

## APPENDIX D

## PARTS LIST FOR AIR POLLUTION SAMPLER FIELD KIT

## CONTRACT SAPH-68345

| ITEM | DISTRIBUTOR | SPECIFICATIONS | NO. or AMOUNT | PRICE (each) | PRICE |
|---|---|---|---|---|---|
| Unistrut - channel | Unistrut | P-6000, 13/16" x 13/16" | 8 ft. | .20/ft. | 1.60 |
| -90° fitting | Pittsburgh | P-6332 | 1 | .31 | .31 |
| -90° fitting | Service | P-6331 | 1 | .31 | .31 |
| -90° fittings | Company | P-6068 | 2 | .12 | .24 |
| -90° fittings | | P-6326 | 2 | .16 | .32 |
| -flat plate fittings | | P-7324 | 2 | .16 | .32 |
| -90° fittings | | P-6728 | 2 | .31 | .62 |
| -Unistrut nuts | | P-6006-1420 | 20 | .31 | 6.20 |
| -Hex Head Cap Screw | | 1/4" x 3/4" | 24 | .03 | .72 |
| -Hexagonal Nuts | | 1/4" | 20 | .02 | .40 |
| Dry Gas Meter | Rockwell | Model 150 | 1 | 43.90 | 43.90 |
| Female Swivels | Mfg. Co. | 3/4" NPT | 2 | | |
| Dewar Flask,St.St. | Superior Air Prod. Co. | 3-1/2" inside diameter 14" inside depth | 1 | 69.04 | 69.04 |
| Helium-Cylinder | Matheson Co. | Size 4, 9 cu. ft. | 1 | 21.00 | 21.00 |
| -Automatic Pressure Regulator | | No. 1, single stage | 1 | 30.00 | 30.00 |
| Filter, Inst. Line | Mine Safety Appl. | 1/4" NPT female connect. | 1 | 10.00 | 10.00 |
| Powerstat | Cameradio | Type 10 115V, 50-100-150 W. | 1 | 8.50 | 8.50 |
| Pump, "Oil-Less" | Gast Mfg.Corp. | Model AD 440-2, 115V 60 cyc. motor | 1 | 61.00 | 61.00 |
| Thermo-Switch | Earl E. | No. 17200, 0-400° brass | 1 | 13.00 | 13.00 |
| Fenwal | Whitaker | No. 17202, 0-600° st.st. | 1 | 15.50 | 15.50 |
| Cartridge Heater, Chromalox | E. D. Wiegand Co. | 200 W, 3/8" O.D. 5" lg. | 1 | 5.20 | 5.20 |
| Tubing, Stainless | Williams & Company | 1/4" O.D. | 10 ft. | 1.65/ft. | 16.50 |
| | | 1/8" O.D. 316 | 2 ft. | 1.15/ft. | 2.35 |
| | | 3/4" O.D. Weldrawn | 2 ft. | 3.45/ft. | 6.90 |

PARTS LIST FOR AIR POLLUTION SAMPLER FIELD KIT (Continued)

CONTRACT SAPH-68345

| ITEM | DISTRIBUTOR | SPECIFICATIONS | NO. or AMOUNT | PRICE (each) | PRICE |
|---|---|---|---|---|---|
| Swagelok Fittings | Fogleman | | | | |
| -Male elbows | Company | 400-2-4 T-1/4", P-1/8" | 3 | 3.77* | 11.31 |
| -All tube tees | | 400-3 T-1/4" | 3 | 3.07 | 9.22 |
| -Bulkhead unions | | 400-61 T-1/4" | 2 | 5.52 | 11.05 |
| -Male connectors | | 400-1-2 T-1/4", P-1/4" | 6 | 1.39 | 8.38 |
| -Male connectors | | 400-1-4 T-1/8", P-1/4" | 2 | 1.45 | 2.90 |
| -Reducing union | | 400-6-2 T-1/4", Tx-1/8" | 1 | 3.15 | 3.15 |
| -Reducer | | 200-R-4 T-1/8", Tx-1/4" | 1 | 2.76 | 2.76 |
| -Caps | | 1210-10 T-3/4" | 4 | 5.26 | 21.06 |
| -Caps | | 400-10 T-1/4" | | 1.17 | 4.68 |
| Hoke Valves, Swagelok Ends | Hoke, Inc. | 303 S. S. Teflon Pack | 2 | 10.40 | 20.80 |
| Dahl "Demi" Valves | Sentinel Products Co. | 303 St.St. Crawford Swagelok 1/4" parts | 2 | 8.54 | 17.08 |
| | | Mounting brackets | 2 | .55 | 1.10 |
| Rotameters, Brooks-Mite | M.S. Jacobs Assoc. | Size 2, 0.2- 5.0 CFH | 1 | 13.00 | 13.00 |
| | | Size 4, 1.0-10.0 CFH | 1 | 13.00 | 13.00 |
| Aluminum Bar Stock | Williams & Co. | 2" x 2" x 6" | 2.5 lbs. | 1.34/lb. | 3.35 |
| Tru-O-Seals | Flick-Reedy Corp. Tru-O-Seals Div. | 1/4" NPT | 5 | .30 | 1.50 |
| | | 1/8" NPT | 6 | .29 | 1.62 |
| Switch, DPST | Cameradio | 125 V, 6 amp. | 2 | 1.00 | 2.00 |
| Fuse Holder | Cameradio | 18 amp., 9/32" dia. x 1/4" | 1 | .41 | .41 |
| Light, Indicator | Cameradio | 110/125 V ac/dc 1/2" Mount | 1 | .57 | .57 |
| Connector, elect. | Cameradio | male 3 pole | 1 | .25 | .25 |
| | | female | 1 | .27 | .27 |
| Plywood | Any Lumber Company | 5-ply 5/8" th. 20" sq. | 1 | 1.20 | 1.20 |
| Plexi-glass | Bell Plastics | 3/16" th., 10" x 20" | 1 | 1.80 | 1.80 |
| Job Charges | Machine Shop | Al. bar stock | 2 hrs. | 6.00/hr. | 12.00 |
| | Glass Blower | Drying tube | 1 hr. | 5.80/hr. | 5.80 |
| | Glass Blower | Solder Swagelok fitting | 1 hr. | 5.80/hr. | 5.80 |
| | | | | TOTAL COST | $489.49 |

* These prices are less 35% discount.